# CHEMISTRY OF POLY(ETHER-ESTER) AND SILOXANE BASED THERMOPLASTIC ELASTOMERS

BY

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To my wife, Maria Helena and the fruit of our love, our daughter Tania.

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ABSTRACT
Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

CHEMISTRY OF POLY(ETHER-ESTER) AND SILOXANE BASED THERMOPLASTIC ELASTOMERS
By

Hector Fabio Zuluaga

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This dissertation deals with thermoplastic elastomers. Specifically it describes alanine mediated polyesterification as well as the synthesis of siloxane graft copolymers with lactones and lactams.

A model study of alanine (ALA) mediated polyesterification was carried out using pivalic acid (PVA) and 2-(2-methoxyethoxy)ethanol (MEEtOH) as model compounds. The effect of alanine on the rate of esterification and on the catalytic activity of titanium tetrabutoxide (TTBO) was examined. Simultaneous reactions with alanine and with combinations of alanine and TTBO were compared with a control reaction of PVA and MEEtOH. While alanine showed a 3- to 6-fold enhancement of the rate of

esterification of PVA with MEEtOH, a small enhancement of the catalytic activity of TTBO was observed. The work was extended to transesterification reactions using methyl benzoate (MeBz) and MEEtOH as model compounds and this time no "alanine" effect was observed.

The synthesis of siloxane graft copolymers with lactones (pivalolactone, γ-valerolactone, δ-valerolactone) and ε-caprolactam led to graft copolymers in all cases except for γ-valerolactone. This work included the introduction of a carboxyl functional group in the siloxane which was used to initiate grafting by ring opening polymerization of the lactone or lactam. The reaction with pivalolactone proceeded at room temperature in tetrahydrofuran and 18-crown-6, while the polymerization of δ-valerolactone required higher temperatures (90°C). Polymerization of ε-caprolactam was carried out in two steps, first heating the reagents in a sealed tube to 260°C and then heating to 180°C under nitrogen atmosphere.

Siloxane graft copolymers with pivalolactone and ε-caprolactam showed a high degree of microphase separation and formed good films from hexafluoroisopropanol solutions. Grafts with different compositions of pivalolactone were prepared, which could lead to the production of thermoplastic elastomers. Siloxane-caprolactam graft copolymers, with siloxane contents up to 18% were synthesized; however, only those copolymers containing 1-4 w% siloxane afforded films. These films showed a siloxane rich surface, and thus the corresponding material is effectively a surface modified nylon.

# CHAPTER 1
# INTRODUCTION

## A Brief Introduction on Elastomers

This dissertation deals with polysiloxane and polyether-based thermoplastic elastomers obtained by combining a *soft* polymeric segment with a *hard* polymeric segment yielding either a block or a graft copolymer. The work has been divided in three parts:

1- Study of the role of alanine in esterification and transesterification reactions using model compounds. This study stems from the promising results obtained in the alanine mediated polyesterification of a poly(ester-ether) telechelomer.

2- Synthesis of siloxane-pivalolactone graft copolymers. A polysiloxane has been substituted for the polyether as the soft segment in the previouly synthesized poly(ester-ether), and a change from linear to graft copolymers was carried out.

3- Substitution of different lactones and lactams for pivalolactone as the hard phase.

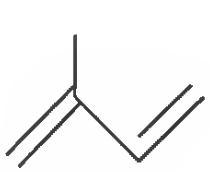
Most materials exhibit some degree of elasticity upon stress, ranging from a very small value for metals to a very large value for rubber. This difference is due to the fact that while metals are made of very well packed atoms, rubber and rubberlike materials are high molecular weight polymers which because of the length of their chains, can adopt a large number of spatial arrangements.

Alteration of these arrangements explains the amazing response of these materials to an imposed stress.

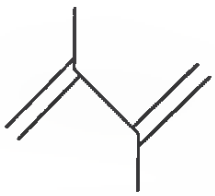
One of the first materials to exhibit a sizable elasticity was discovered by the American Indians, who called it *caoutchouc*, from *caa* wood and *o-chu* to flow or weep, because it was obtained as a milky sap by making incisions on the trunk of the tree *Hevea brasiliensis*.[1] The Europeans discovered a number of uses given to this material by the Indians: they spread it on clothes to make them waterproof; they produced gumboots, flexible bottles and enema syringes, etc.[1] Rubber products, however, suffered from two major drawbacks: first, the gum was sticky and remained permanently sticky at room temperatures. In hot weather it turned softer and stickier; second, in cold weather it became progressively hard and stiff, and in extreme frost, it became almost completely inflexible. A solution to this problem was found by an American inventor, Charles Goodyear,[2] who discovered the process now known as vulcanization. Introduction of vulcanization on both sides of the Atlantic was followed by the rapid successful application of rubber to virtually all of its modern uses. The climax came with the patenting of the pneumatic tire in 1888 by John B.Dunlop;[1] his invention came just at the right time to meet the needs of the infant automobile industry.

The large demand for rubber over the next few years was an incentive for the search of a synthetic substitute. It was already known that rubber was made of isoprene (1), Figure 1.1, which was converted to rubber by Bouchardat[3] in France, Tilden in England and Wallach[4] in Germany. Eventually F. Hofmann[5] in Germany succeeded

in synthesizing isoprene from mineral sources and, in 1909, was awarded the world's first patent for a synthetic rubber.[6] By this time, Kondakov in Russia had discovered that dimethylbutadiene (2) could be converted into an elastic polymer and was more easily obtained.[7]



Isoprene (1)



Dimethylbutadiene (2)

Figure1.1. Structures of isoprene and dimethyl-butadiene.

World War I put an end to further developments in England, while in Germany, cut off from natural supplies, the effect was the opposite and research was accelerated by the Nobel prize winning discovery of Staudinger that rubber was made up of giant molecules.[8]

Summarizing, the requirements needed for a rubberlike material to be useful are as follows: 1- the material must consist of polymeric chains; 2- the chains must have a high degree of flexibility; 3- the chains must somehow be joined into a network structure.[2]

The first requirement arises from the fact that the molecules in an elastomeric material must be able to alter their arrangements and extensions in space dramatically in order to respond to an imposed stress, and only long-chain molecules have the required

large number of spatial arrangements of very different extensions. Figure 2 shows a two-dimensional projection of a random arrangement of a 200 carbon polyethylene chain.[9]

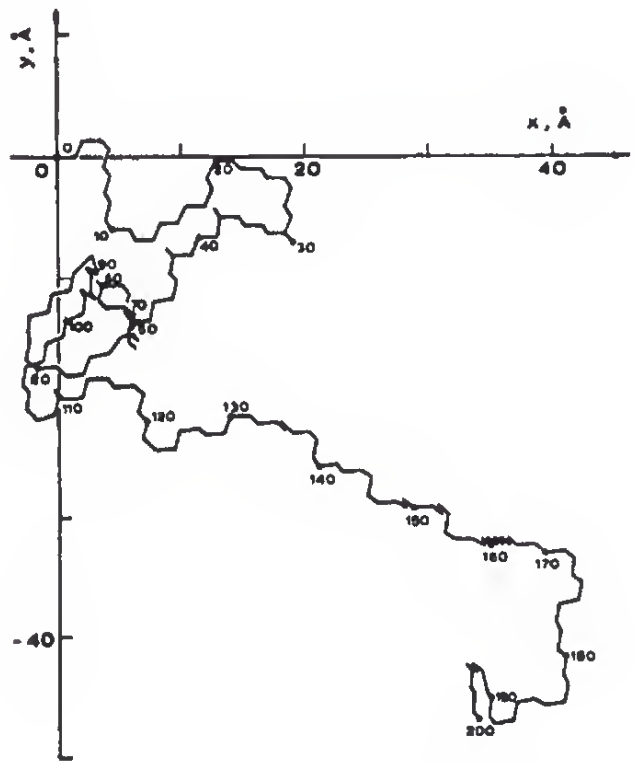



Figure 1.2. Two-dimensional drawing of a 200 carbon polyethylene chain.

This projection was generated by using well known bond lengths and bond angles, and by considering the preference of n-alkanes for trans rotational states. Two features of this projection are worth mentioning, these being (a) the high extension of part of the chain, due to the preference for trans conformations and (b) the tendency of some sections of the chain to fold in a random fashion,

forming more compact zones that decrease the end-to-end distance of the chain. Even for this short chain, the extension could be increased to 400% by rotation around the skeletal bonds without altering bond angles nor breaking bonds.[9]

When an elastic polymer is stretched, the elastic work, W, can be expressed as[10] :

$$W = fdx$$

where

f = retractive force

dx = change in length

If the change in the free energy is $\partial G$,

$$(\partial G/\partial X)_{T,P} = (\partial H/\partial X)_{T,P} - T(\partial S/\partial X)_{T,P}$$

An ideal elastomer is defined by the condition

$$(\partial H/\partial X)_{T,P} = 0 \qquad f = -T(\partial S/\partial X)_{T,P}$$

The equation above shows that the retractive force in an ideal elastomer is due to the decrease of entropy on extension, which originates in the distortion of the polymer chains from their more probable conformation.

The second requirement specifies that the different spatial arrangements be accessible, not hindered by intrinsic rigidity of the chains, extensive degree of crystallization, or high viscosity. This needed flexibility implies that the polymer not only should be in its amorphous state but, at use temperature, should be above its glass

transition temperature, Tg, in order to overcome the brittleness characteristic of the glassy state.

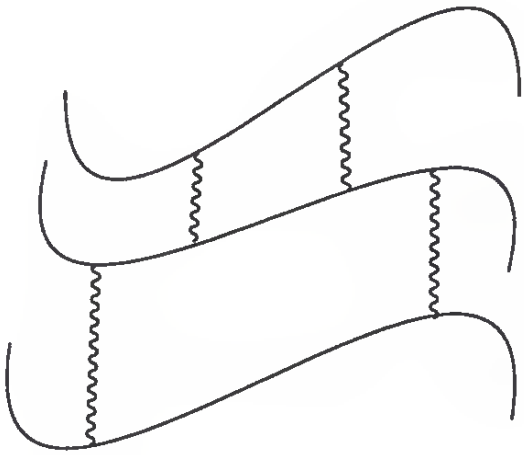


Figure 1.3. Cross-linked polymer chains.

The third characteristic is required in order to obtain the elastomeric recoverabilty. It is obtained by joining or *cross-linking* segments of the chain, Figure 1.3, thereby preventing stretched polymer chains from irreversively sliding by one another.

The Discovery of Elastic Copolymers

A new development in rubberlike materials was the discovery that copolymers of dienes and olefins yielded better elastomers than polydienes or polyolefins alone. One of the first to be prepared was a copolymer of butadiene and styrene, similar to but not identical to the styrene butadiene rubber of today.[11] Now with the experience gained over the years and a good understanding of the kinetics and mechanism of copolymerization, polymer chemists are able to

synthesize products with predetermined properties. By carefully choosing the components of a copolymer, the properties of the respective homopolymers can be modified at will. The modification of the polymers also can be achieved by mixing or blending them with other materials which are effective in altering behaviour such as antioxidants, plasticizers, flame retardants, fillers, etc. When the additive is a high molecular weight polymer the resulting mixture is called a *polymer blend*. A blend is a physical mixture of two or more polymers as opposed to a copolymer, which posesses a chemical bond between its components. Most blends are not stable however, because of unfavorable free energy considerations. Polymers prefer to intertwine among themselves rather than among other polymers, and as a consequence, they eventually separate into different phases.[12]

In a mixture of polymers a very small entropy of mixing ($\Delta S$) is observed, and even a slight positive change of enthalpy ($\Delta H$), is sufficient to produce a positive change in free energy; thus incompatibility of the two polymers results.

Polymer blends can be useful when molecular weights are low or when the expected useful life of the product is relatively short, and therefore a simple mixture of polymers might be perfectly suitable to achieve a specific property. On the other hand if mixtures can be co-reacted, such as cross-linking of two unsaturated rubbers, very useful long term behaviour results and the product is really a copolymer.

Copolymers can be classified as (a) random, (b) alternating, and (c) block, Figure 1.4.

~~AAABBAABAABBBABBAA~~ random copolymer

~~ABABABABABABABABAB~~ alternating copolymer

~~AAAAAAAAABBBBBBBBB~~ block copolymer

Figure 1.4. Classification of copolymers

Random copolymers are the product of a statistical placement of the comonomers along the chain. A copolymer is considered perfectly random when the two monomers show equal reactivity to both propagating species. For example, methacrylonitrile (3) and methyl methacrylate (4) have very similar reactivity ratios under radical polymerization[13] and consequently they react under these conditions to produce a random copolymer, as shown in Figure 1.5.

Alternating copolymers result from the alternate placement of the comonomer along the chain. This type of copolymer requires pairs of monomers with very low reactivity ratios (no affinity for their own propagating species). An example is the free radical copolymerization of styrene (5) and maleic anhydride (6). The most generally accepted mechanism for this reaction[14-15] suggests the formation of 1:1 complexes of an electron donor (styrene), and an electron acceptor (maleic anhydride), which react to produce an alternating copolymer, Figure 1.6.

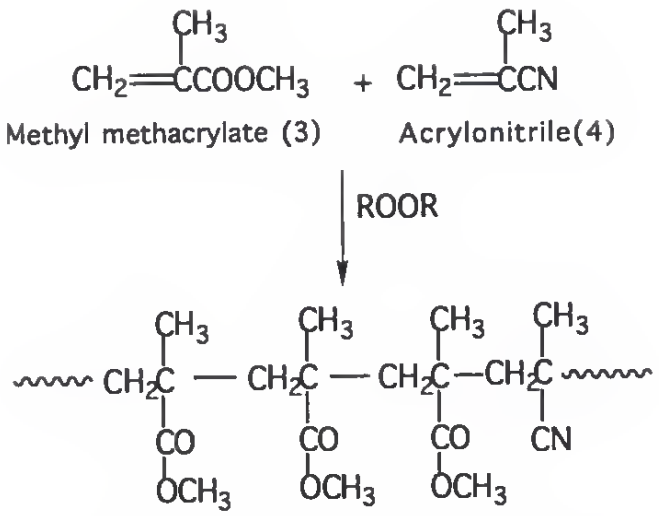



Figure 1.5. Production of a random copolymer from methacrylonitrile and methylmethacrylate

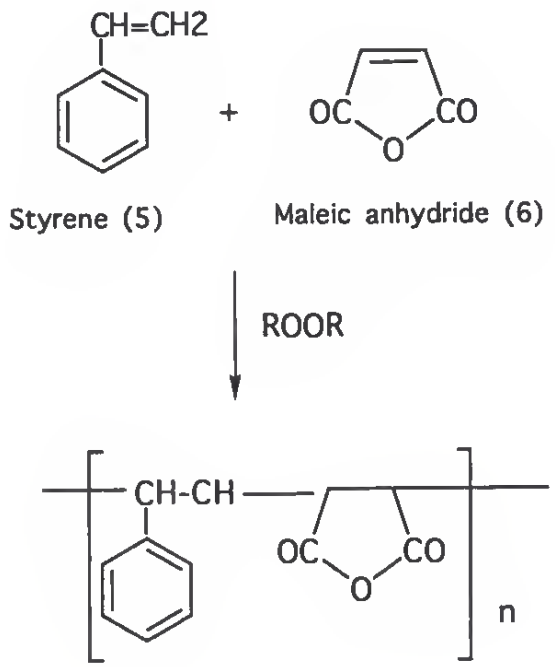



Figure 1.6. Formation of an alternating copolymer from styrene and maleic anhydride.

Block copolymers are comprised of terminally connected segments of comonomers. They are synthesized by "living" addition polymerization or by step growth condensation techniques. A-B and A-B-A architectures are primarily synthesized by anionic living polymerization, while -(-A-B-)-$_n$ structures are more often prepared by step growth methods. Anionic living polymerization , discovered by Szwarc and coworkers,[16] allows control of molecular weight and molecular weight distribution by fixing the monomer to initiator ratio, while the order of addition of the monomers determines the sequence of the blocks. The synthesis of an A-B-A, styrene-butadiene- styrene block copolymer is shown in Figure 1.7.

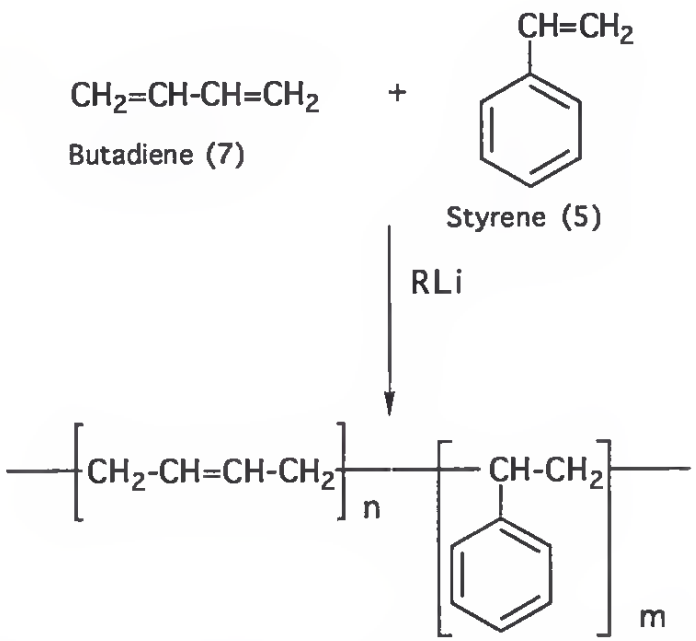



Figure 1.7. Synthesis of styrene-butadiene-styrene.

In the mid 1980's a combination of living anionic polymerization and ring opening polymerization was employed to

synthesize a polyether-ester telechelomer with an OH group at one end and a COOH group at the other. This prepolymer was polymerized by step growth condensation, to obtain a multiblock or segmented copolymer with $(A\text{-}B)_n$ architecture.[17-18] The synthesis of this segmented copolymer will be discussed in detail later.

Graft Copolymers

The copolymers displayed so far are all linear. Graft copolymers, on the other hand, Figure 1.8, consist of a functionalized, linear backbone to which a second monomer has been attached, as a side chain, via chemical bond with the functional group.

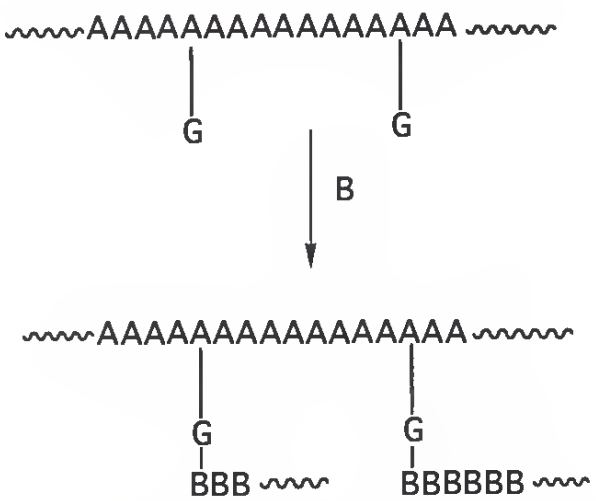



Figure 1.8. Formation of graft copolymers.

Graft copolymers are generally prepared by free radical, anionic, cationic or ring opening polymerization. Free radical graft copolymerization is based, for the most part, on the reaction of

olefinic monomers in the presence of preformed polymers containing labile hydrogens.[19] The reaction is initiated by peroxides, irradiation or thermal methods.[20] Abstraction of the reactive hydrogen produces radicals on the backbone which can polymerize the second monomer. Graft copolymers prepared by this method are characterized by a poor control on the composition.

Ionic methods allow better control of the structure, especially when living anionic techniques are used. If the first polymer backbone is functionalized with several anionic sites and the second monomer is copolymerized by living techniques using the anionic functional group as initiator, excellent control of the structure of the graft can be achieved. This is the case when the cyanopropyl group in poly(dimethyl-co-methylcyanopropylsiloxane) is converted to the carboxylate and then reacted with pivalolactone[21] (8) to obtain polypivalolactone chains as pendants from the polysiloxane backbone, Figure 1.9. The advantage of this synthesis is twofold. First, carboxypropyl units are randomly placed on the polysiloxane, due to similar reactivities in the two monomers, dimethyldichlorosilane (9), and methylcyanopropyldichlorosilane (10), and the carboxylic acid concentration on the backbone, can be controlled by the ratio of the two monomers. Second, the living ring opening polymerization of pivalolactone (8) proceeds easily at room temperature and the amount of pivalolactone grafted can be controlled as well. The combination of an amorphous polysiloxane backbone with a highly crystalline segment may lead to very special properties of the product as will be discussed in the next section.

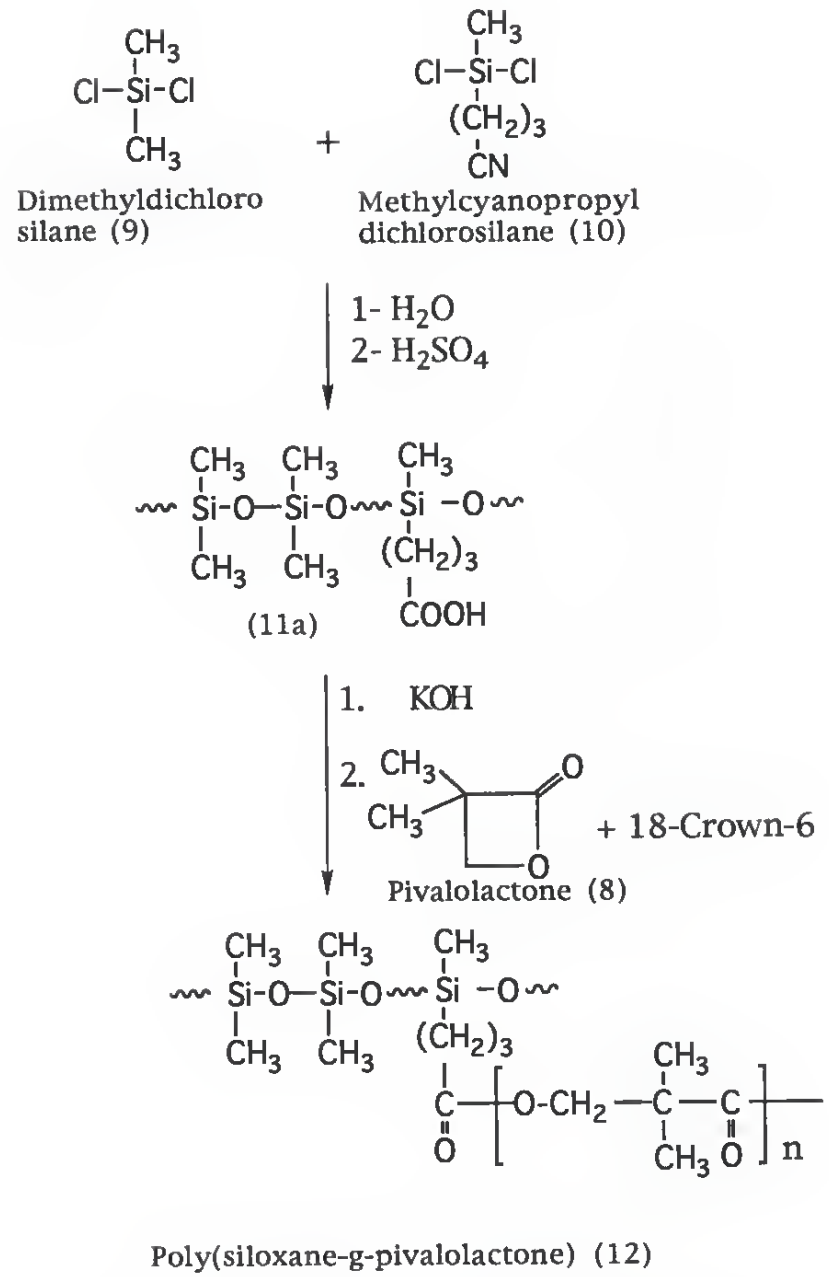



Figure 1.9. Synthesis of poly(siloxane-g-pivalolactone)

## Thermoplastic Elastomers

Thermoplastic elastomers are materials with rubber-like behaviour that soften and can be reshaped upon heating. In the late 1940s, Coleman at ICI attempted to improve the dyability of polyethyleneterephthalate, PET, by copolymerizing it with poly(oxyalkylene)glycol.[22] A similar approach was used by Snyder at Dupont[23] to increase PET hydrophilicity; he carried out a controlled ester interchange by melt mixing PET with a copolymer of terephthalic acid, trimethyleneglycol and suberic acid. The resulting copolyester had a higher strength, a higher stretch modulus than any natural rubber threads and a very quick elastic recovery (snap). The fibers were regarded as thermoplastic elastomers since they could be extruded from their melt or spun from solvents.

An important discovery was made by Schollenberg and coworkers at Goodrich,[24] who reported on a polyurethane elastomer, *Estane*,™ which is a linear polyurethane described as being "virtually cross-linked" by secondary rather than primary forces. At Shell, di and triblock copolymers of styrene-butadiene and of isoprene-styrene were successfully made in 1957 by Porter.[25] During subsequent work at this company, it was observed that "unvulcanized" styrene-butadiene-styrene, S-B-S, triblock copolymers, were unusually "snappy" and appeared to be "scorched"; stress-strain measurements showed high tensile strength and high ultimate elongation, while solution data showed complete solubility with no gel or microgel formation.[22] This anomalous behaviour led

to the formulation of the domain theory.[27-30] This theory considers that in the bulk state, the polystyrene short end segments of these block copolymers agglomerate; at temperatures significantly below the glass transition temperature of polystyrene, these agglomerations (domains) act as strong, multifunctional junction points, and so the triblock copolymers behave as though they are joined in a cross-linked network.[22]

Thermoplastic elastomers have been widely studied; the poly(urethane-ether) thermoplastic elastomers discovered by Schollenberg and Scott[24] in 1958 which have been the subject of intense research in the following years,[31,32] are synthesized by step polymerization of an aryl diisocyanate (13) and a diol (14), see Figure 1.10. Other thermoplastic elastomers obtained by step condensation polymerization are poly(ester-ethers),[33] polyamides,[34] and polysiloxane copolymers.

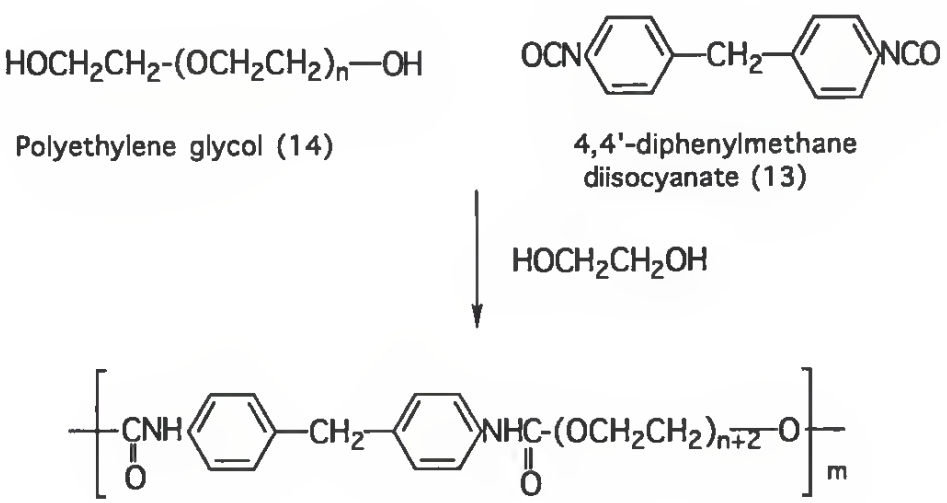



Figure 1.10. Poly(urethane-ether) thermoplastic elastomer.

Poly(siloxane) copolymers can be used as elastomers at very low temperature due to the low glass transition of the siloxane phase. Some examples of siloxane materials include copolymers with polyurethanes,[35] polycarbonates,[36] polymethacrylates,[37] polyamides,[38] polymethylstyrene[38] and polypeptides.[39] Only a few of them possess a semicrystalline phase, which in many respects is preferred for thermally induced changes. Other advantages of the siloxanes copolymers are biocompatibility, chemical inertness, gas permeability, hydrophobicity and low surface energy. This last property is very important for the synthesis of surface modified polymers.

## Microphase Separation

The different constituents of block and graft copolymers are bonded together covalently, thereby preventing inmiscibility of the constituents from leading to physical separation as described earlier. However, they show very special properties as a result of morphological features unique to these systems. These features have been explained by the domain theory in terms of "microphase" separation of the incompatible components. The resulting microphases, hard and soft segments, are of a size on the order of the dimensions of the constituent polymer molecules themselves, and these microphases often develop a highly organized domain morphology.

A pictorial representation of microphase separation is given in Figure 1.11; the hard segment acts as a physical cross link while the soft segment is responsible for the elastic behaviour. This idealized

structure was postulated[22] from the mechanical and rheological properties of S-B-S triblock copolymer but there was no direct observation to support it. Although microphase separation had clearly been established by the Strasbourg School,[40-42] the phenomenon remained a curiosity until Holden and Milkovich[27] discovered that microphase separation in block copolymers, of appropiate composition and architecture, could yield materials with unique and useful properties.

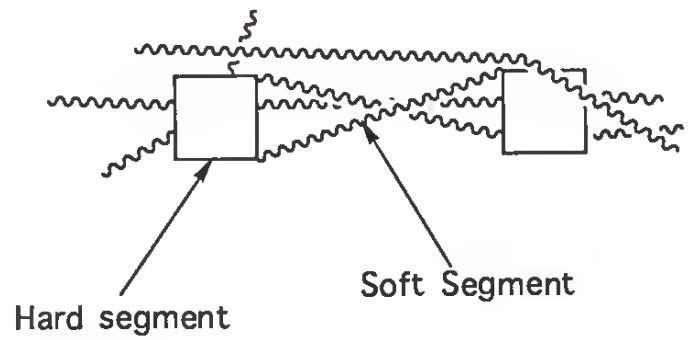



Figure 1.11. Representation of the microphase separation in a block copolymer.

The development of staining techniques using osmium tetroxide[43] allowed morphologies to be established by electron microscopy.[44] Using these techniques a more detailed picture of the morphological changes with block copolymer composition was proposed,[45] as shown in Figure 1.12. Three basic types of morphology for microphase separated copolymers are possible: spheres, cylinders and alternating lamellae. As the styrene content increases, the morphology of the polystyrene phase changes from spheres to cylinders, both dispersed in a continuous diene phase.

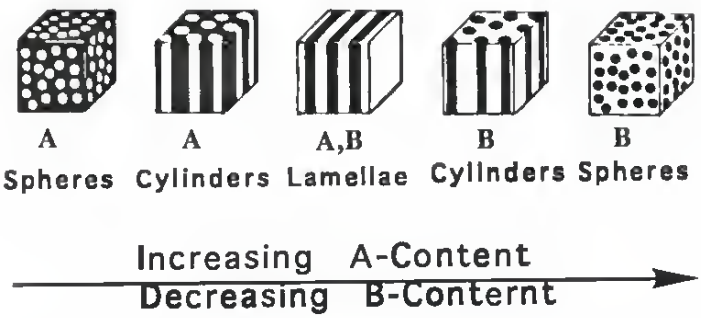



Figure 1.12. Effect of composition on block copolymer morphology.

When the volume fraction of styrene and diene are about the same, the two form alternating lamellae. Further increase in polystyrene content reverses the situation and now cylinders and spheres of the diene appear in a polystyrene continuous phase.

Microphase separation in $(A\text{-}B)_n$ type multiblock copolymers, is only observed if one of the segments is crystalline.[46] Few studies on microphase separation have been performed for graft copolymers. Depending on their chain structure and homogeneity, graft copolymers can have multiphase morphologies similar to A-B, A-B-A, or $(A\text{-}B)_n$. [47-49]

Differential scanning calorimetry (DSC) has been very useful in the study of microphase separation. The degree of phase mixing is indicated by the deviation on a thermal transition such as glass transition (Tg) and melting temperature (Tm). The presence of separate values of Tg or Tm coinciding with those of the respective homopolymers is an indication of good phase separation. Other

techniques employed to study phase separation in copolymers include electron microscopy (EM), small angle X-ray scattering (SAXS), and dynamic mechanical analysis (DMA).

Using DSC[50,51] it was found that with a poly(pivalolactone) segment length constant at 12 units, microphase separation begins when the poly(oxyethylene) segment contains 14 units and is complete upon extension to 24 units, (Figure 1.13). If the poly(oxyethylene) unit is kept constant at 24 units and the PVL is varied, $(PVL)_m$-$(POE)_{24}$-$(PVL)_m$, a small degree of microphase separation is observed for m= 5,7,9; complete microphase separation is achieved when m reaches 16.

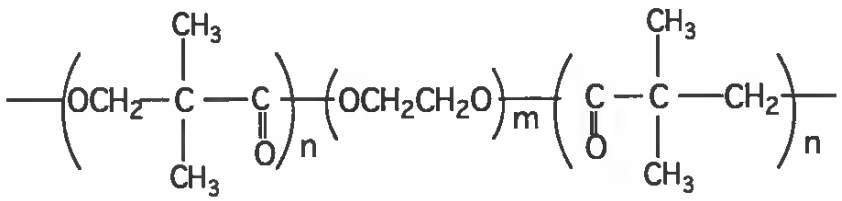


Figure 1.13. Structure of pivalolactone-polyoxyethylene triblock copolymer (15).

Therefore, copolymers with segmental composition: $(PVL)_{12-16}$-$(POE)_{14-24}$-$(PVL)_{12-16}$, or higher, show excellent phase separation.

## Thermoplastic Elastomers Via Chain Propagation/Step Propagation Polymerization

As described above polymer architecture can be varied to achieve well phase separated, solvent resistant poly(ester-ether) copolymers,[17-18] Figure 1.14. Even so true poly(ester-ether)s are

deficient in terms of the physical properties that are required in many applications, particularly when they are melt processed.[52] Deficiencies in properties such as elastic recovery (less than 95%), stress decay (often greater than 15%) and compression set (more than 10%) are manifestations of the inefficiency of the physical cross-link, which in turn is a result of poor phase separation. Phase mixing can be attributed partly to irregularity of the polymer chain.

In the case of poly(ester-ether) copolymers prepared by step condensation polymerization, the hard segment has a polydispersity ratio approaching 2, and this broad molecular weight distribution adversely affects phase separation.[53] Therefore high regularity within segments, i.e. monodispersity within each segment, should lead to enhanced phase separation and better crystallization phenomena.[54] Furthermore, the model study mentioned before[50,51] supplies information on the length of the POE and PVL blocks necessary to ensure good phase separation.

A block copolymer from the soft segment ethylene oxide (16), and the hard segment pivalolactone (8), was synthesized by anionic living techniques, ensuring monodispersity within each segment. Since the soft poly(oxyethylene) segment is incompatible with the hard poly(pivalolactone) segment, these regular copolymers exhibit enhanced phase separation. On the other hand, high molecular weight is necessary to obtain a thermoplastic elastomer with good mechanical properties. In order to further polymerize this block copolymer by step growth propagation the carboxyl group provided by polypivalactone on one end and the hydroxy group provided by

polyoxyethylene at the other end have been used, making the difunctionalized block copolymer a telechelomer.

Figure 1.14 illustrates the approach used to synthesize the poly(oxyethylene-b-pivalolactone) telechelomer (20).[17,18] An acetal capped anionic initiator[21] (17) polymerizes ethylene oxide to give a potassium alkoxide of a masked polyether and this new initiator is used to polymerize pivalolactone. Since potassium alkoxides are strong nucleophiles, they can randomly attack the carbonyl carbon and the β-methylene carbon in lactones. Such a random attack would result in a pivalolactone segment containing irregularities. A weaker nucleophile such as carboxylate anion will attack the β-methylene carbon of pivalolactone.[55-57] Thus it became necessary to convert the alkoxide end to a carboxylate anion by reacting (19) with succinic anhydride (18). The carboxylate anion was used to polymerize pivalolactone (8) yielding the masked poly(oxyethylene-b-pivalactone) copolymeric salt (19). Acid hydrolysis converted this salt to the telechelomer, $(POE)_n$-SA-$(PVL)_m$, (20), where n=29, m=12.

Polymerization of this telechelomer by step growth condensation was attempted using different -OH and -COOH activating agents, and polyesterification catalysts.[18] However, none of the attempts were successful. High polymer was finally achieved by alanine in a first "activation" step at 180°C, followed by an increase in temperature to 250°C using $Ti(OBu)_4$ , a known transesterification catalyst. It is the first time that alanine has

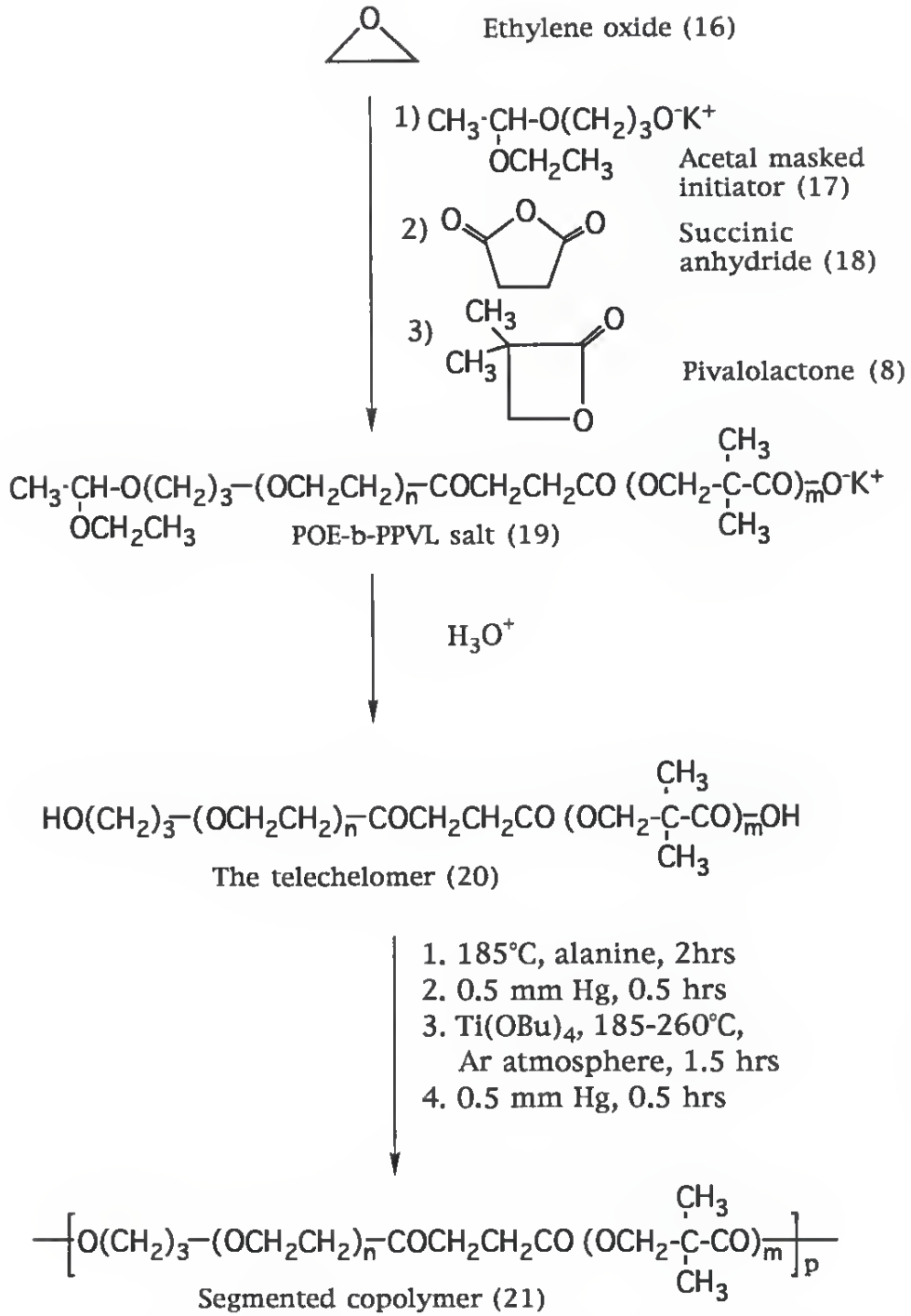



Figure 1.14. Chain propagation/step propagation polymerization of ethylene oxide and pivalolactone.

been used as an activator for polyesterification, and a more detailed study of the "alanine effect" has been undertaken in this dissertation.

## Polysiloxane Based Thermoplastic Elastomers

Some of the advantages of polysiloxanes as the soft phase in thermoplastic elastomers have already been mentioned in this chapter. More detailed information may be found in the review on siloxane containing copolymers by Yilgor and McGrath.[58]

A series of poly(siloxane-g-pivalolactone) copolymers were synthesized[59] in order to investigate composition/phase separation relationships, and phase separation studies were carried out by DSC.

Table 1.1. DSC data of poly(siloxane-g-pivalolactone).

| PVL | PDMS | PPVL |
|---|---|---|
| W% | Tg (°C) | Tm (°C) |
| 10 | -123 | 187.7 |
| 20 | -123 | 191.1 |
| 30 | -123 | 201.5 |
| 40 | -123 | 202.2 |
| 50 | -123 | 221.5 |

The results are presented in table 1.1. The Tg for the PDMS backbone was the same for all the compositions of the copolymers and the Tm for the poly(pivalolactone) segment was close to that of homopoly-(pivalolactone) with similar molecular weights. From these results

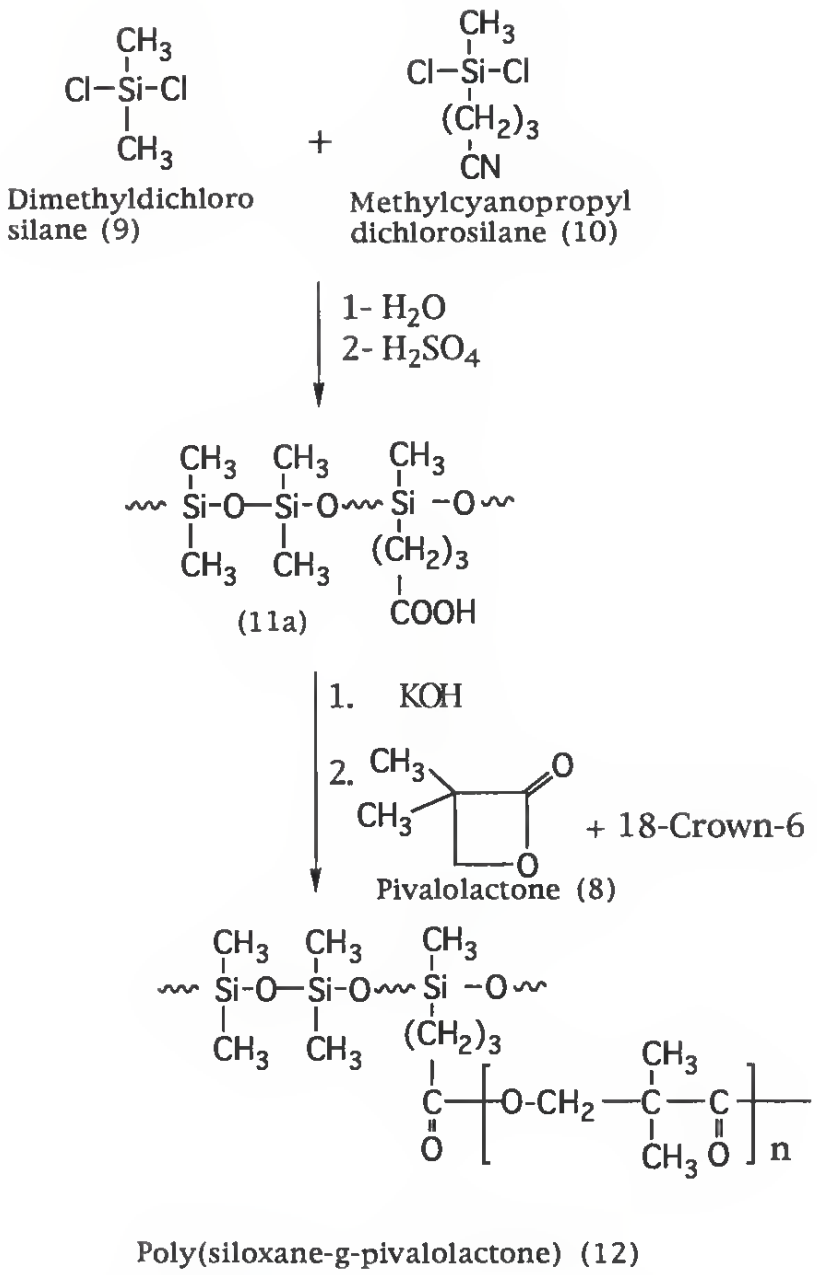



Figure 1.15. Synthesis of poly(siloxane-g-pivalolactone).

it was concluded that there was excellent phase separation in the copolymer with pivalolactone contents up to 60%. Water contact

angle measurements confirm this conclusion, as all copolymers, except those containing 70% poly(pivalolactone), show a surface richer in poly(dimethylsiloxane).

The synthesis of poly(siloxane-g-pivalolactone) is illustrated in Figure 1.15. Cyanopropyl functionalized siloxane copolymers were obtained by hydrolytic polymerization of the respective dichloro silanes (9) and (10). The cyano group was converted to the potassium carboxylate, and this functional group was used to graft pivalolactone to the siloxane backbone.[60, 61]

Patwardhan[60] synthesized a series of carboxypropyl functionalized siloxanes with different spacing of the functional group on the siloxane backbone in order to study the influence of the carboxylic acid functional group concentration. 10, 20, 37, 60, and 120 Dimethylsiloxane repeat units per methylcarboxypropylsiloxane unit were introduced in the backbone by controlling the mole ratio of the two monomers, and grafting of pivalolactone on two of them was carried out.

## Objectives of this Dissertation

This dissertation describes an extension of the work on siloxane based graft copolymers. Other lactones and lactams have been substituted for pivalolactone as the hard phase in order to investigate the influence of the chain length of the lactone monomer on the properties of the graft copoplymer.

The specific objectives of the research described in this dissertation have been to conduct a model study of alanine mediated esterification and transesterification for thermoplastic elastomers

and homopolymers and to synthesize siloxane based thermoplastic elastomers grafted with new lactones and lactams as a hard phase.

For the first time, alanine has been reported to act as an "activator" in polyesterification. This is a very interesting result, as polyesterification is one of the most commercially exploited reactions in the world, and as a consequence, large quantities of different catalysts are consumed in the polymer industry. Many of those catalysts are expensive and some of them are toxic; on the other hand, alanine is a natural product, and nontoxic. It will not only be more economical but will also be an environmental alternative in the production of polyesters.

The synthesis of well phase separated, biocompatible, and solvent and radiation resistant, siloxane based graft copolymers that could be used as thermoplastic elastomers, is the other subject of this dissertation. The research has been focussed in two aspects, these being control of the molecular weight of the siloxane soft phase and substitution of other lactones and lactams for pivalolactone as the hard phase. Control of the molecular weight of the segments is highly desirable in order to assure good phase separation, which is necessary for the synthesis of thermoplastic elastomers. Figure 1.16, illustrates the synthesis of the siloxane graft copolymers with lactones and lactams.

The soft segment is synthesized by acid catalyzed ring opening of octamethylcyclotetrasiloxane (22) and its methylcyanopropyl analog (23). This is an equilibrium reaction, where the linear polysiloxane can regenerate cyclic siloxanes by backbiting, Figure 1.17. A decrease in the amount of cyclics can be obtained if the end

groups are blocked by reacting them with a monofunctional disiloxane.

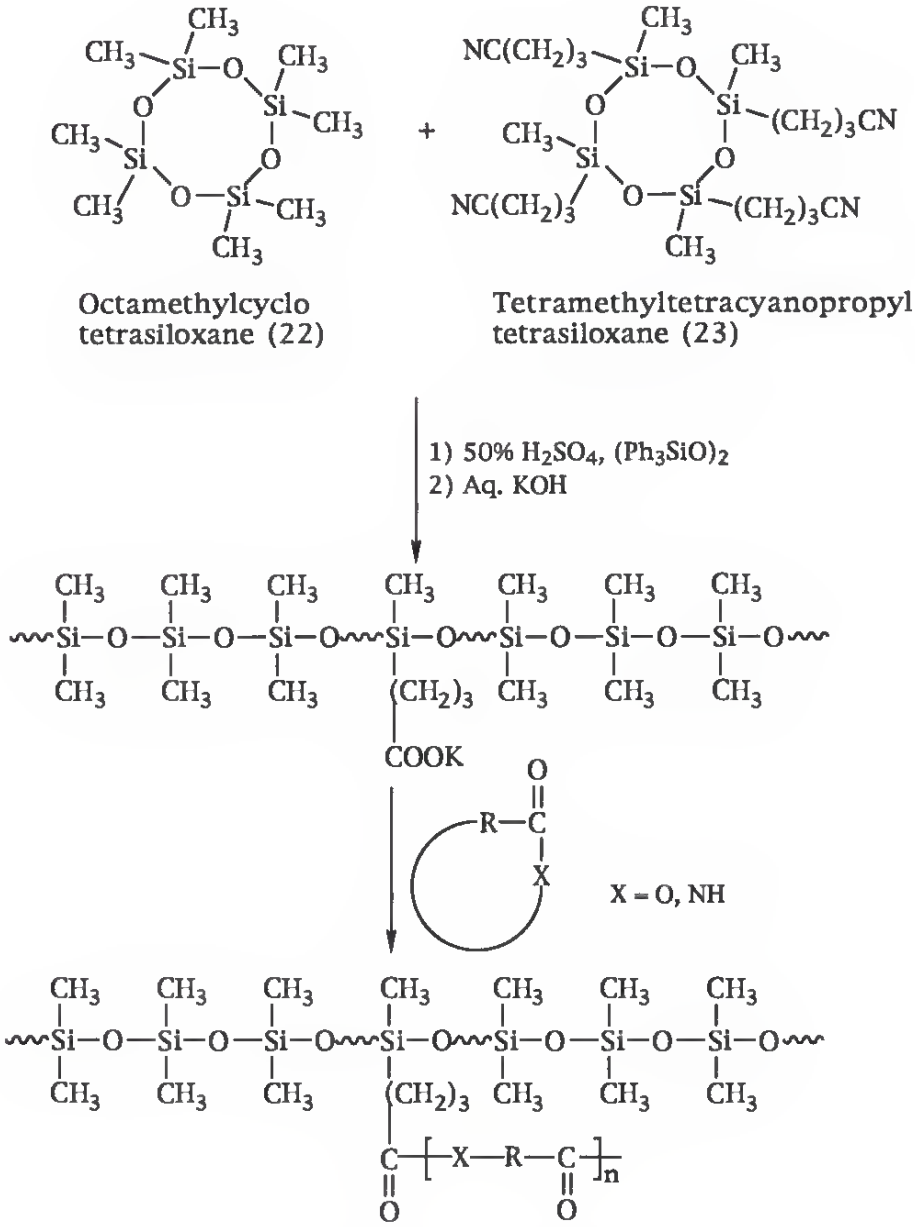



Figure 1.16. Synthesis of polysiloxane graft copolymers with lactones and lactams.

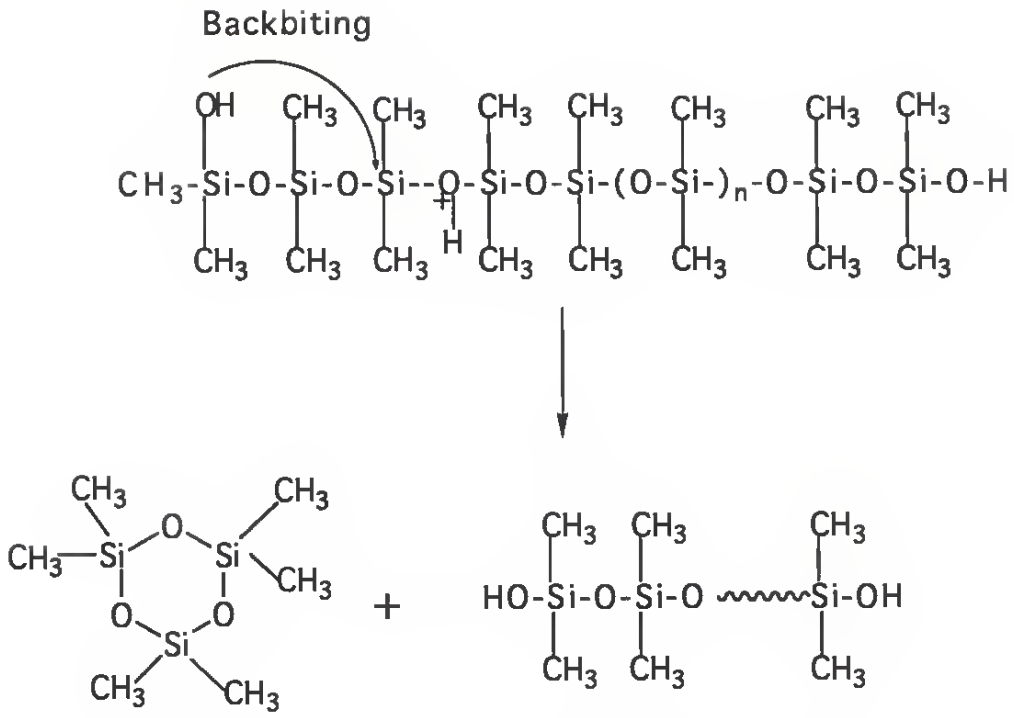



Figure 1.17. Backbiting to form cyclics.

Hexaphenyldisiloxane not only acts as an end capper which blocks backbiting, but it also permits molecular weight determination by $^{1}H$ NMR. Correlation with other methods such as vapor pressure osmometry (VPO), GPC, and viscometry allows a better insight into molecular weight variations.

All these topics will be discussed in the chapters that follow.

# CHAPTER 2
# ALANINE MEDIATED POLYESTERIFICATION

Polyester elastomers are multiblock segmented copolymers which can be represented by the general formula $-(A-B)_n-$. Commercialization of polyester elastomers has led to extensive research in this area and, because these polymers offer unique physical properties and processing characteristics, they have gained worldwide acceptance.[61] Any contribution that could lead to new catalysts will be of academic and commercial interest. Before discussing the study on the role of alanine in esterification, some background information will be presented.

## Introduction to Polyesterification

Polyesters have been studied since the last century,[62] but it was not until the 1930s that Carothers[63] carried out a systematic study on polyesterification; he prepared a series of linear aliphatic polyesters that did not find commercial use due to their low melting points. In 1946, Whinfield[64] prepared poly(ethyleneterephthalate), PET, and it was at this time that polyester became widely used for the manufacture of fibers and films. In order to have commercial application a polyester has to have high molecular weight, regular chemical structure, and adequate physical properties to allow processability. The synthesis of a particular polyester can often be

successfully performed by different methods: in bulk (usually at high temperature), in solution, by an interfacial method or in the solid state.[65] When performed at low temperature, either in solution or by an interfacial method, polyesterification may present problems related to the removal of residual catalyst, side products, or solvent. When polymerizations are carried out at high temperature, chain scission may compete with the growing chain reactions, an event which can become the most important limiting factor for the molecular weight to increase.[65]

Industrial production of polyester is carried out by direct esterification, figure 2.1, or by transesterification, figure 2.2.

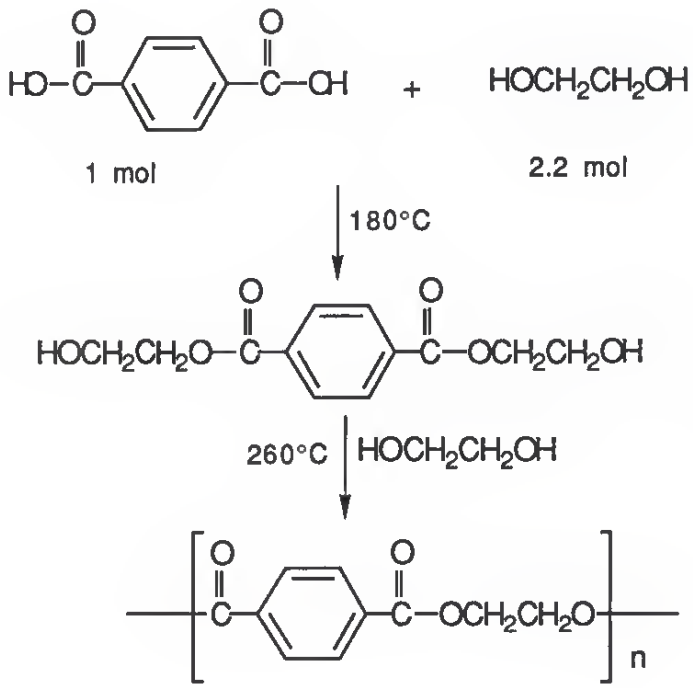



Figure 2.1. Synthesis of "polyester" by direct esterification.

Most polyesterification reactions only occur at sufficiently high rates in the presence of suitable catalysts, and due to the academic and industrial relevance of catalysis, an enormous number of publications have appeared.[65]

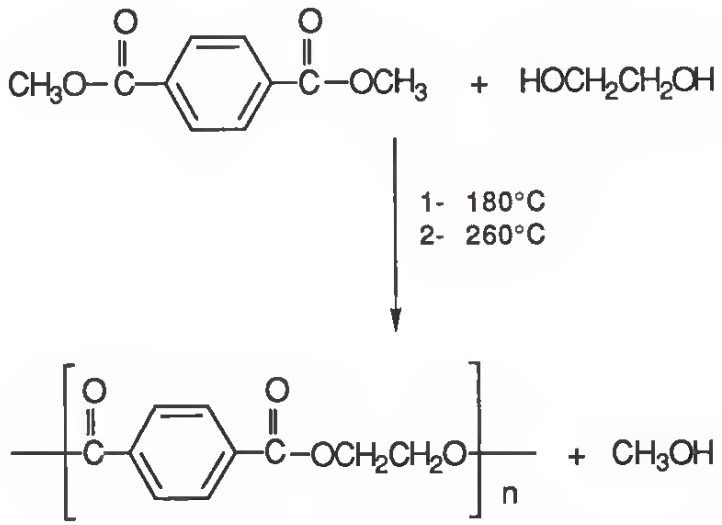



Figure 2.2. Synthesis of "polyester" by transesterification.

Most polyesters can be obtained by direct esterification at high temperature either from dicarboxylic acids and diols or from hydroxy acids. Esterification is an equilibrium reaction that can be driven to completion by removal of the water produced in the process. The reaction is normally carried out under reflux, where water is removed by either application of vacuum to the system or by the introduction of a stream of an inert gas.

Direct esterification can proceed at high temperature (180°C-280°C) even in the absence of added catalysts; in this case the carboxyl group of the acid provides protons that catalyze the

reaction. Small amounts (0.1-0.5 wt %) of an external catalyst are nevertheless added in order to increase the reaction rate . An extensive list of catalysts employed in direct esterification has been reported by Fradet and Marechal.[66] This list includes strong protonic acid such as $H_2SO_4$, $H_3PO_4$, $CF_3SO_3H$, p-toluensulphonic acid, etc., oxides or salts of heavy metals, and organometallic compounds of titanium, tin, zirconium and lead. It appears that for a metal to be effective it has to be able to exchange ligands and to coordinate with reactants forming a complex that it is not too strong. The catalytic activities of many metal compounds have been compared, and it has been found that alkoxide derivatives of titanium and zirconium are the most efficient.[67]

Most of the polyesters made by direct esterification can also be prepared by transesterification. This reaction is of great commercial importance, since monomers as ester derivatives have lower melting points, higher solubilities in diols, and can usually be obtained at a higher purity grade than the corresponding acids, and therefore often allow production of better quality products and easier process control. However higher costs, resulting from more expensive raw materials and more expensive plants, sometimes makes direct esterification more convenient, as in the case of PET.[68]

Alanine Mediated Polyesterification of a Hydroxyacid Telechelomer

A recent study of polyesterification catalysis can be found in the synthesis of well phase separated thermoplastic elastomers combining chain and step propagation polymerization.[17-18] This

synthetic scheme was presented in figure 1.14, where the chain propagation process involved the use of an acetal masked initiator to polymerize ethylene oxide, followed by reaction with succinic anhydride to yield a carboxylate terminated oligomer. Addition of pivalolactone to this oligomer, followed by hydrolysis, produced a monodisperse poly(oxyethylene-b-pivalolactone) telechelomer (20) having a Mn of 2700 and containing -OH and -COOH end groups.

Subsequent step propagation of this hydroxy acid terminated telechelomer was attempted without any success, even when the telechelomer was treated with -OH and -COOH activators. COOH activating agents such as N,N'-bis(2-oxo3-oxo-azolidinyl)-phosphoramidic chloride/triethylamine,[69] 1-methyl-2-bromo-pyridinium chloride/tri n-butylamine,[70] and OH activating agents such as triphenylphosphite,[71] hexachlorocyclotriphosphatriazene,[72] and dehydrating agents such as trifluoroacetic acid/methylene chloride and methylsulphonic acid /phophorus pentoxide,[73] had no effect on the polymerization. Well known polyesterification catalysts such as antimony oxide and titanium tetrabutoxide also did not induce step polymerization.

The use of alanine followed by titanium tetrabutoxide, figure 2.3, yielded a high molecular weight $-[(POE)_n-(PVL)_m]_x$ multiblock segmented copolymer (20).[18] Surprisingly, alanine was almost totally recovered via sublimation when the telechelomer/alanine mixture was subjected to vacuum (0,5 mmHg). Furthermore, elemental analysis of the copolymer (21), revealed the presence of 0.1% nitrogen, indicating a catalytic amount of alanine left in the product. The theoretical amount of nitrogen calculated on the basis

of a 1:1 reaction of the telechelomer and alanine is 0.5%, and thus it is evident that alanine did not form a 1:1 adduct with the telechelomer.[18] This is the first time that an amino acid of natural ocurrence has been reported as an activator for polyesterification and, if confirmed, it could be of great commercial value as a substitute for antimony and titanium based catalysts which present a certain degree of toxicity.

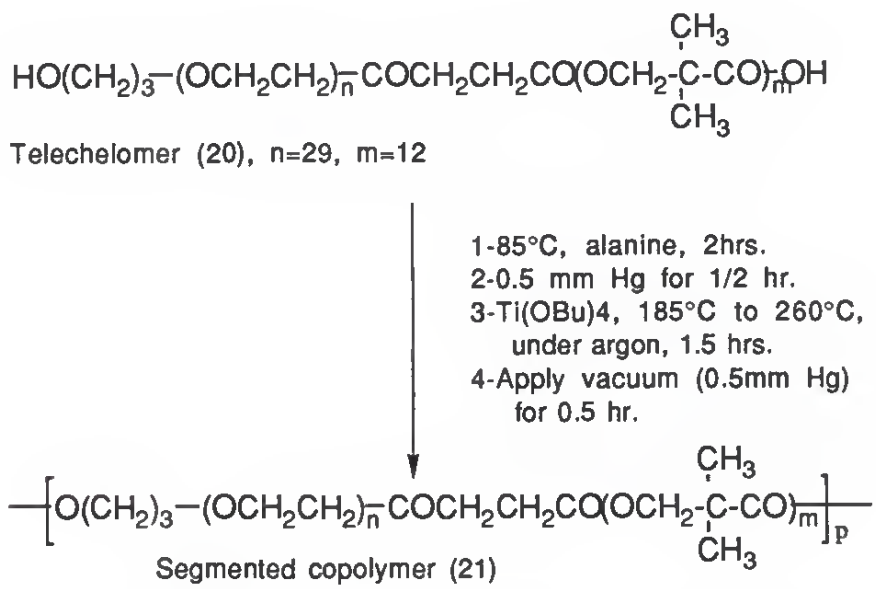

HO(CH2)3–(OCH2CH2)n–COCH2CH2CO(OCH2-C(CH3)2-CO)m–OH
Telechelomer (20), n=29, m=12
1-85°C, alanine, 2hrs.
2-0.5 mm Hg for 1/2 hr.
3-Ti(OBu)4, 185°C to 260°C, under argon, 1.5 hrs.
4-Apply vacuum (0.5mm Hg) for 0.5 hr.
Segmented copolymer (21)

Figure 2.3. Alanine mediated polyesterification of the telechelomer.

The selection of alanine (24) as a possible "activator", was aimed at the alleviation of the steric hindrance posed by the two methyl groups α to the carboxyl end group of the telechelomer, assuming that an amide linkage is to be formed,[18] see figure 2.4. If the copolymer is on average a tetramer of the telechelomer, then 0.1% N in the copolymer is approximately equivalent to a 1:1

alanine:copolymer adduct, a fact overlooked previously. This suggests that alanine (24) reacts with the growing chain to form either an amide (25), or a mixed anhydride (26). Propagation of this reaction would require a second molecule of the telechelomer to perform a nucleophilic attack on either the amide or the anhydride derived from the first telechelomer molecule.

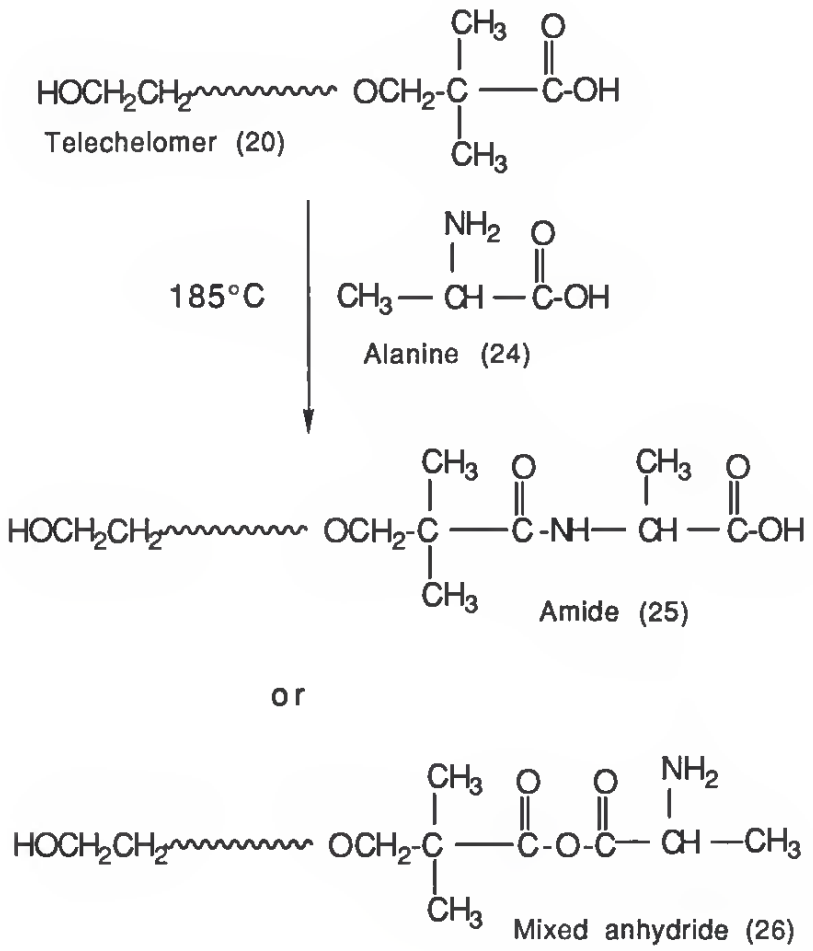



Figure 2.4. Reaction of alanine with the telechelomer

These derivatives are even more sterically crowded on the site of propagation than the telechelomer, and therefore the steric reasons invoked as the argument for using alanine could be neglected.

The fact still remains that the only way to convert the telechelomer to the segmented copolymer involved the use of alanine in a preliminary step and three hypotheses can be proposed as a possible explanation for the action of alanine in this reaction. a) Alanine could simply act as a dehydrating agent; b) It could act as a template for the two reacting ends of the telechelomer, c) It could increase the effectiveness of $Ti(OBu)_4$ catalyst itself.[18]

The first hypothesis seems reasonable, as alanine is known to form a dimer upon heating with the loss of two molecules of water. It may well be that when alanine sublimes as a result of the vacuum applied, figure 2.3, the dimer regenerates alanine monomer, carrying water out of the system.

The second hypothesis requires that alanine bring two telechelomer molecules together in such a way that the carboxyl end group of one molecule finds the hydroxyl end group of the other. This implies a high degree of order in the chains, which at this temperature, 185°C, and given the length of the telechelomer is unlikely.

The third hypothesis is not very reasonable, as the catalytic action of titanium alkoxides implies coordination of the carboxylic acid to the titanium and exchange of alkoxide groups for the hydroxyl group.[67] A telechelomer alanine adduct would in fact place the carboxyl group further away from the coordination center.

It seems more reasonable to consider that in forming the mixed anhydride with the telechelomer, alanine becomes a better leaving group (as the carboxylate) rather than the hydroxyl group. Furthermore, hydrogen bonding of the amino group of the mixed anhydride with the carbonyl of the telechelomer could help labilize the carbonyl for the nucleophilic attack of the OH end group of another chain (figure 2.5). Similar hydrogen bonding could be true in the amide intermediate; however, the amide group is not as good leaving group.

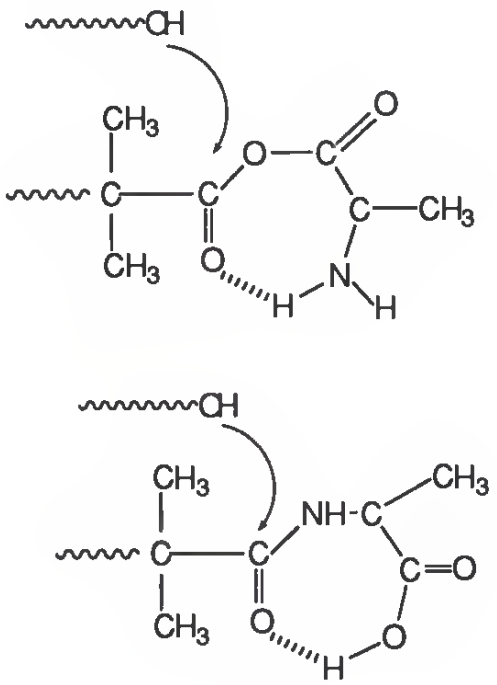


Figure 2.5. Hydrogen bonded assisted nucleophilic attack of the hydroxyl end on the carboxyl end of the intermediate.

A model study was undertaken in order to investigate the specific role of alanine in this process.

A Model Study of Alanine Mediated Esterification

Model studies help to determine if a reaction that has been successful under specific conditions can be generalized to a whole class of compounds holding the same functional groups. In the present case, the telechelomer (20) can be considered a hydroxy acid, and its polymerization yields a polyester.

Pivalic acid, PVA, and 2-(2-methoxyethoxy)-ethanol, MEEtOH, were chosen as model compounds in an attempt to mimic the chemistry involved in the synthesis of the telechelomer, see figure 2.6.

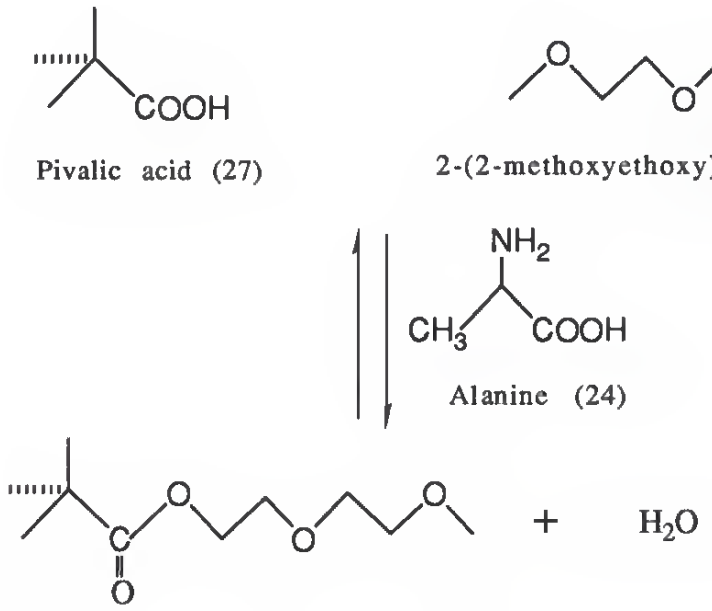



Figure 2.6. Alanine mediated esterification of model compounds.

Pivalic acid (27) is similar to the pivalolactone hard segment of the telechelomer, and 2-(2-methoxyethoxy)ethanol (28) is equivalent to three ethylene oxide (soft segment) repeat units. If alanine is a catalyst in the polymerization of the telechelomer (20) to a multiblock segmented copolymer (21) then a rate enhancement in the model reaction should be observed. Could alanine be a catalyst for polyesterification in general? A second model study to mimic formation of polyethyleneterephthalate is presented as well.

Esterification of Pivalic Acid

The reactions were carried either under vacuum or under argon atmosphere. In each case the reagents were dried under vacuum at room temperature, and then heated until they refluxed; samples were syringed out and analyzed by high performance liquid chromatography (HPLC).

Reactions under vacuum

1- The effect of alanine alone.

Simultaneous reactions with and without alanine under moderate vacuum (0.1 mm Hg) and reflux (93-124°C) were carried out. Comparison of the retention factor (Rf) of the reaction mixture by thin layer chromatography (TLC) with the Rfs of the starting materials showed the increase of ester (29) with time as confirmed by infrared spectroscopy (IR) and $^{13}C$ nuclear magnetic resonance, ($^{13}C$ NMR). The change in the carbonyl stretching frequency in the IR, from 1696 to 1725 $cm^{-1}$, as well as the change in the $^{13}C$ NMR chemical shift from 183 to 178 ppm indicated the conversion of pivalic acid (27) to the corresponding ester (29), (figures 2.7 and

2.8). Furthermore, quantitative analysis of the reaction mixture was carried out by high performance liquid chromatography, HPLC, which allowed calculation of the ester acid ratio. Table 2.1 shows a 4-6 fold catalytic effect by alanine on the esterification reaction.

Table 2.1. Ester/acid ratio vs time for alanine mediated reactions.

| Time | Reaction number | | |
|---|---|---|---|
| (h:min) | 1 | 2 | 3 |
| 1:10 | 0.06 | 0.25 | 0.56 |
| 2:10 | 0.23 | 0.43 | 1.10 |
| 3:30 | 0.59 | 0.67 | 2.40 |
| 5:40 | 0.61 | 0.99 | 4.30 |
| 8:05 | 0.93 | 1.00 | 6.70 |

Alanine mol% : reaction 1: 0.0, reaction 2: 5.2, reaction 3: 0.52.

When alanine mole % is 5.2 the rate of the reaction is increased in the first three hrs, but reaches a constant value after that. However when alanine mole% is reduced an order of magnitude to 0.52, all the samples analyzed show a significant increase in the reaction rate.

2-The combined effect of alanine and titanium tetrabutoxide.

According to the work discussed before,[18] the combination of alanine and titanium tetrabutoxide (TTBO) was the key to a successful polymerization of the hydroxy acid telechelomer (20).

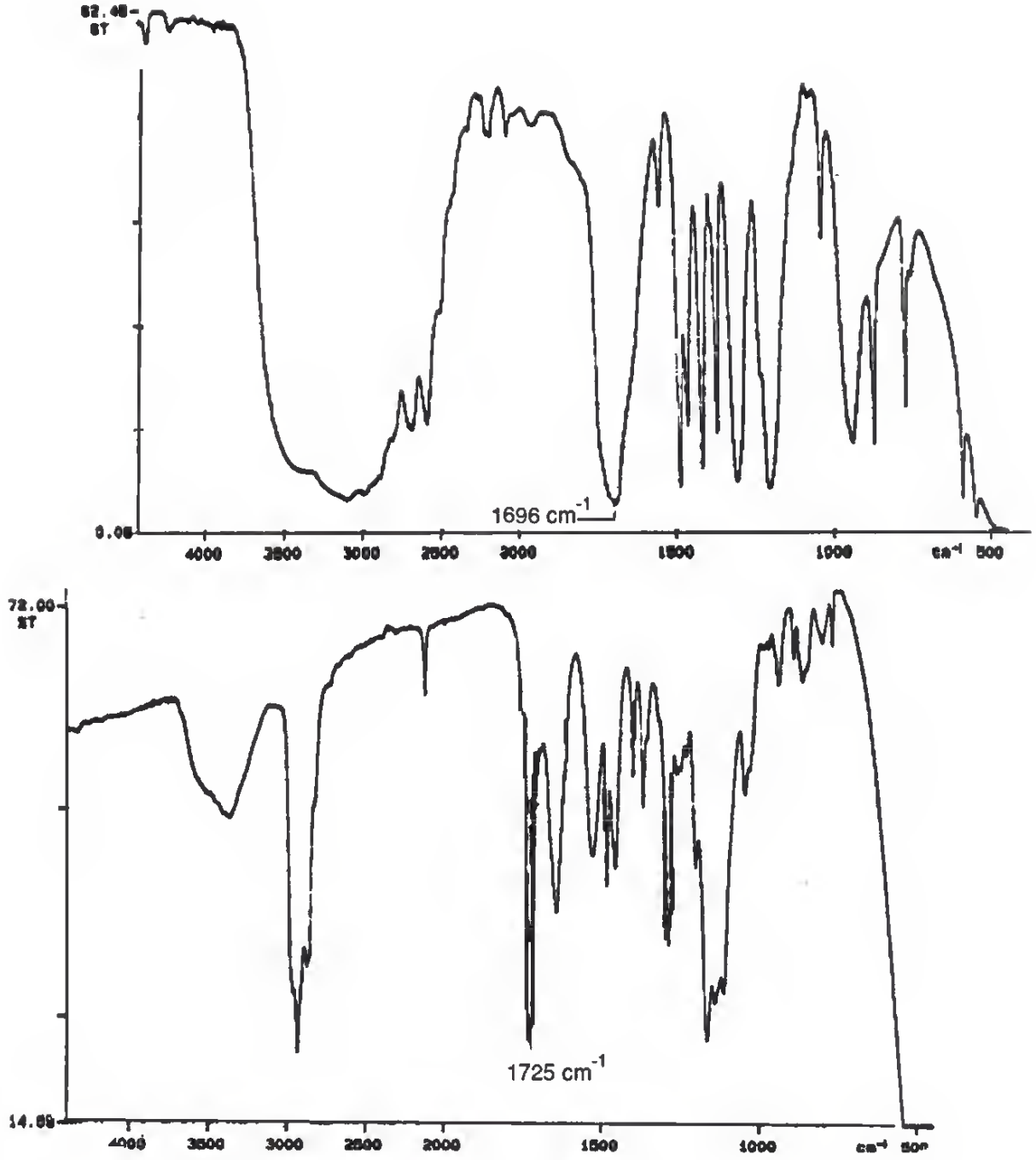



Figure 2.7. IR of pivalic acid, top, and 2-(methoxyethoxy)ethyl pivalate, bottom.

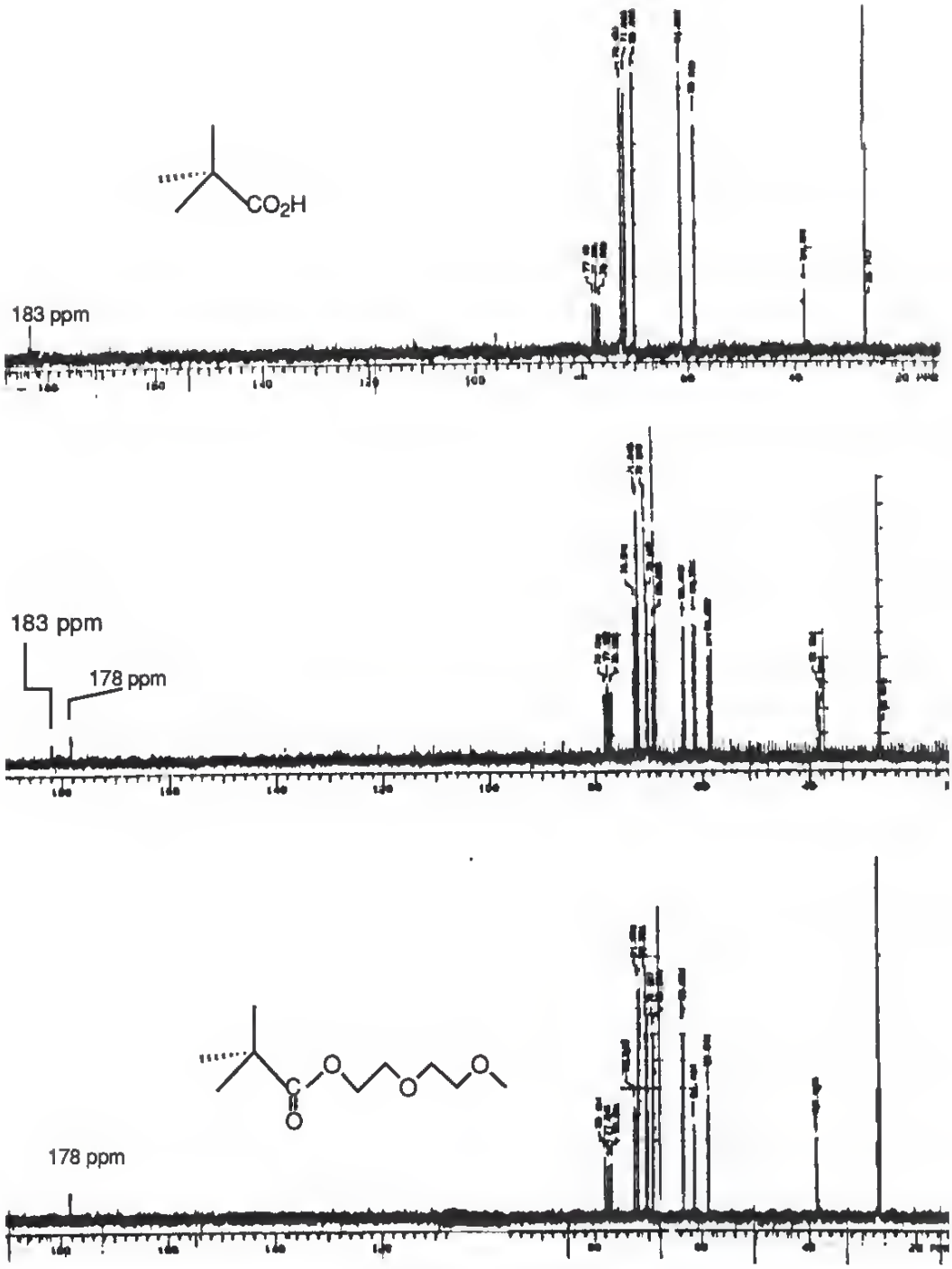



Figure 2.8. 13C NMR of pivalic acid, top, reaction mixture, center, methyl pivalate, bottom.

One of the hypotheses was that alanine could enhance the catalytic activity of titanium tetrabutoxide, and thus experiments were designed to compare the catalytic action of alanine and TTBO separately with the catalytic activity of a mixture of both. In separate experiments, equimolar amounts of pivalic acid and the alcohol (MEEtOH) were treated with 3% molar TTBO and varying amounts of alanine; 6.5 and 1 mole percent alanine was added to the 4th and 5th reactions, respectively, (see table 2.2).

Table 2.2. Ester/acid ratio vs time

| Time | Reaction number | | |
|---|---|---|---|
| (h:min) | 3 | 4 | 5 |
| 1:25 | 1.05 | 0.47 | 0.77 |
| 2:03 | 7.46 | 2.85 | 22.5 |
| 4:05 | 19.2 | 17.0 | 100 |

Alanine, TTBO mole%: reaction 3: 0.0, 3.1; reaction 4: 6.5, 2.9; reaction 5: 1.0, 3.0.

While the presence of 1% alanine showed a 1-3 fold increase in the production of the ester with respect to the control, the presence of 6.5% alanine had just the opposite effect. This result indicates that alanine in amounts close to 1.0% enhances the catalytic activity of TTBO. Confirmation of this "alanine effect" was obtained when three separate reactions, each one with 1.5% TTBO and varying alanine mole % of 0.0, 1.0 and 1.0, were run simultaneously. The reactions containing 1.0% alanine, showed a 1-3 fold increase in the production of the ester (table 2.3). These encouraging results led us

to carry out reactions with catalyst concentrations similar to those used in industrial polyesterification in order to explore potential commercial applications.

Table 2.3. Ester/acid ratio vs time.

| Time | Reaction number | | |
|---|---|---|---|
| (h:min) | 7 | 8 | 9 |
| 1:08 | 0.10 | 0.15 | 0.30 |
| 4:00 | 0.34 | 0.47 | 0.43 |
| 8:05 | 0.60 | 1.90 | 1.50 |
| 12:30 | 0.70 | 2.60 | 13.1 |

Alanine, TTBO mole%: reaction 7: 0.0, 1.5; reaction 8: 1.0, 1.5; reaction 9: 1.0, 1.5.

The amount of titanium tetrabutoxide used in the industrial production of polyethyleneterephthalate PET is of the order of 0.1-0.05 mole %, however, reactions using this amount of catalyst were very slow. As expected, an increase in the amount of catalyst to 1.4% reduced reaction times to those observed in previous experiments. However, the "alanine" effect was not observed and further experiments did not always reproduce the earlier findings.

This research then leads to three conclusions: 1- Molar concentrations of alanine close to 1.0% appear to enhance the rate for esterification of pivalic acid with methoxyethoxyethanol 2- In order to observe catalytic activity of titanium tetrabutoxide its molar concentrations should be close to 1.0%. 3- At low pressure (0.1-10 mm Hg) and relatively low temperatures (70-110°C), alanine

concentrations close to 1.0% molar appear to produce a small enhancement of titanium tetrabutoxide catalytic activity.

Model reactions under argon

Further esterification experiments were carried out, this time under argon atmosphere, just above atmospheric pressure, allowing study of the reactions at higher temperatures.

The reagents were dried under vacuum at room temperature, then mixed and heated to reflux temperatures (160-170°C). Samples were syringed out from the reactions and analyzed by HPLC. Table 2.4 shows the results obtained when three separate reactions were run; reaction 10 contained no alanine nor TTBO, reaction 11 contained 0.75% TTBO, and reaction 12 contained 0.75% TTBO and 1.0% alanine.

Table 2.4. Ester/acid ratio vs time.

| Time | Reaction number | | |
|---|---|---|---|
| (h:min) | 10 | 11 | 12 |
| 1:00 | 0.24 | 2.2 | 1.9 |
| 1:55 | 0.54 | 3.7 | 2.6 |
| 2:20 | 0.41 | 3.9 | 2.9 |
| 2:50 | 1.0 | 5.0 | 3.5 |
| 3:20 | 1.4 | 5.8 | 4.2 |
| 3:58 | 1.8 | 7.0 | 4.5 |
| 4:50 | 3.2 | 7.4 | 4.8 |
| 9:00 | 3.6 | 18 | 7.0 |

Alanine, TTBO mole% : reaction 10: 0.0,0.0; reaction 11: 0.0, 0.75; reaction 12: 1.0, 0.75.

Two interesting observations can be extracted from these data. Esterification reactions are faster when run under argon at higher temperatures. 2- No enhancement by alanine of the catalytic activity of TTBO, was observed under these conditions.

In fact, comparison of tables 2.3 and 2.4 shows that higher ester/acid ratios are observed for reactions under argon at higher temperatures. This, of course, is expected as higher temperatures increase the number of molecules with enough energy to overcome the activation energy of the reaction. The second observation, no "alanine" effect, was contradicted by a similar experiment, where a slight increase in the activity of TTBO was observed when a mixture of 1.2/0.75 mole% alanine/TTBO was added to the reagents.

Finally, a transesterification model study was carried out to complete this work and this research is discussed in the next section.

Transesterification of Methyl Benzoate

One of the problems in the direct esterification of pivalic acid is the precipitation of a white solid attributed to hydrolysis of titanium alkoxides.[67] Transesterification of methyl pivalate was not feasible due to its low boiling point (101-102°C), and therefore methyl benzoate (b.p. 198-199°C) was chosen as a suitable model compound. Besides its higher boiling point, methyl benzoate has a very close resemblance to dimethyl terephthalate, the most used monomer in the polyester industry, and the side product of the reaction, methanol, is easier to remove (b.p. 64-65°C).

Since previous esterification of pivalic acid proceeded at a higher rate when carried out at atmospheric pressure and refluxing temperatures, the same conditions were applied to the following experiments.

Equimolar amounts of methyl benzoate (MeBz) and 2-(2-methoxyethoxy)ethanol (MEEtOH) were reacted under argon atmosphere; refluxing temperatures started at 150°C and increased to 190°C as the transesterification proceeded to completion. Four reactions were carried out (table 2.5); when 1.2 mole % alanine was added, no positive effect on the reaction rate was observed. Addition of 0.71 mole % of TTBO instead of alanine, produced a positive effect at the beginning but after 3 hours no enhancement of the reaction rate was observed.

Twelve more reactions were completed after modification of the apparatus in order to establish identical conditions for all the experiments. Two of these experiments showed the "alanine" effect, while the other 10 did not not exhibit this phenomenon.

Table 2.5. MEETBz/Me Bz ratio vs time.

| Time | Reaction number | | | |
|---|---|---|---|---|
| (h:min) | 13 | 14 | 15 | 16 |
| 0.40 | 0.05 | 1.9 | 2.6 | 0.02 |
| 1:50 | 0.35 | 2.6 | 3.3 | 0.94 |
| 3:20 | 2.2 | 3.0 | 3.5 | 1.7 |
| 4:20 | 8.3 | 5.1 | 3.6 | 1.9 |
| 6:40 | 18 | 5.7 | 3.8 | 2.4 |

Mole % alanine, TTBO: reaction 13: 0.0, 0.0; reaction 14: 1.2, 0.71; reaction 15: 0.0, 0.71 ; reaction 16:.1.2, 0.0.

These results led us to conclude that alanine does not enhance the catalytic activity of TTBO in the transesterification of methyl benzoate and MEEtOH.

It should be noted that the conditions in the step propagation of the telechelomer could not be reproduced exactly with model compounds. The telechelomer was a solid with number average molecular weight (Mn) of 2700, which could be heated to high temperatures under vacuum. The exact conditions of the reactions were as follows: equimolar amounts of d,l-alanine and telechelomer were heated, under argon, to 185°C for two hours, then, maintaining the temperature, the reaction was switched from 760 mm Hg to 0.1 mm Hg for 1/2 hour; at this point alanine sublimed and was withdrawn from the reaction mixture. The product obtained did not form a film when cast from a solution in methylene chloride. Addition of a catalytic amount of TTBO to this product and heating to 185°C, under argon, produced a highly viscous polymer which could not be magnetically stirred. Finally the temperature was gradually increased to 260°C for 1.5 hours and then vacuum applied for 1/2 hour.

As can be inferred from the previous paragraph, alanine was required in a first step, but then removed and TTBO added as catalyst. Furthermore, low pressure (0.5 mm Hg) and high temperatures can be applied in the second step of the reaction. The application of such conditions was not possible in our model studies due to the volatility of pivalic acid and methyl benzoate. For example, alanine was present all the time in these alanine-mediated

model reactions. Sublimation of alanine was not possible without evaporating pivalic acid or methyl benzoate.

## Conclusions

Model studies for transesterification and esterification have shown that in most cases alanine enhances the rate of esterification of pivalic acid (PVA) and 2(2-methoxyethoxy)ethanol (MEEtOH). Furthermore, alanine appears to enhance the catalytic activity of titanium tetrabutoxide (TTBO) in the same reaction. Alanine may play a role in a preliminary activation step of the polyesterification of poly(pivalolactone)-poly(oxyethylene) telechelomers, as shown by the formation of dimers, trimers and occasionally pentamers of the telechelomers. However, reproduction of the exact conditions of the original reaction was not possible with low molecular weight model compounds.

# CHAPTER 3
# POLYSILOXANE GRAFT COPOLYMERS WITH LACTONES

## Thermoplastic Elastomers Based on Soft Phase-Hard Phase Copolymers

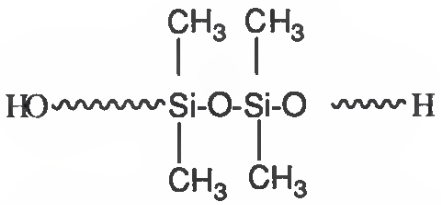
A part of this research has dealt with the catalyzed synthesis of polyester elastomers. This section describes work on siloxane graft copolymers as potential thermoplastic elastomers where one goal has been to improve the thermal stability of a siloxane soft phase and assure its analytical evaluation. A second goal has consisted of examining the effect of ring size of a lactone monomer on the hard phase behaviour.

In view of the promising previous results,[18,59] the synthesis of poly(siloxane-g-lactones) was undertaken in a search for thermoplastic elastomers with good microphase separation, solvent and radiation resistance, and biocompatibility. One of the requirements for the production of thermoplastic elastomers.[27-30] is the display of microphase separation between the hard and soft phases.

The soft phase, responsible for the elasticity, should be a flexible polymer with a low glass transition temperature (Tg) while the hard phase should be either a highly crystalline polymer, or, an amorphous polymer with a high Tg, such that at use temperature, the hard phase is in the glassy state. The hard phase acts as a

physical cross-link that prevents the copolymer chains from slipping past each other.

Polydimethylsiloxanes, figure 3.1, are an excellent choice for the soft phase, due to the unusual molecular structure of the polymer chains themselves.



Polydimethylsiloxane, PDMS, (30)

Figure 3.1. Structure of poly(dimethylsiloxane).

The Si-O bond (1.64Å) is longer than the C-O bond (1.41Å) but substantially shorter than the Si-O predicted by calculation from the atomic radii (1.83Å). This shortening of the bond length can be explained by its large ionic character (40-50%) and by its partially double bond character due to the $p_p$ - $d_p$ interaction between the p lone pair in the oxygen and the empty d orbital in the silicon.[74] The Si-O bond is highly polarized as a result of silicon's low electronegativity (1.74); hence, large intermolecular forces would be expected.

Surprisingly, siloxanes show large molar volume (75,5 cc/mole),[75] low cohesion energy,[76] low surface tension and surface energy, low solubility parameter and low dielectric constant.[74,77] These unusual properties have been explained by Rochow on the basis of a high mobility of the methyl groups and confirmed by

spectroscopic[76] and thermodynamic studies.[74] The polymer's low intermolecular forces and flexibility are also responsible for the low Tg of polydimethylsiloxanes which, together with a high thermal stability, make them unique for their use as elastomers in a very wide temperature range. Additionally, polydimethylsiloxanes are transparent to UV light, very resistant to ozone and atomic oxygen,[74,77] highly permeable to various gases, hydrophobic, and both chemically and physiologically inert.[77,78]

Despite their outstanding properties, polydimethylsiloxanes (PDMS) require high molecular weights to develop useful mechanical properties. Even at molecular weights of the order of $10^6$ they exhibit cold flow and very weak rubbery properties. Chemical cross-linking has been used to improve mechanical properties; however, they still show low tensile and tear strength. A description of silicon rubbers and their many uses can be found in the book by Lynch[79] and references given there.

Noshay and McGrath[80] show that the two preferred general methods for the synthesis of block copolymers are forms of living addition polymerization, or step growth condensation polymerization. Figure 3.2 illustrates an example of living polymerization using butyl lithium as initiator producing a butadiene-dimethylsiloxane diblock copolymer. An example of the step growth condensation polymerization technique is shown in figure 3.3.

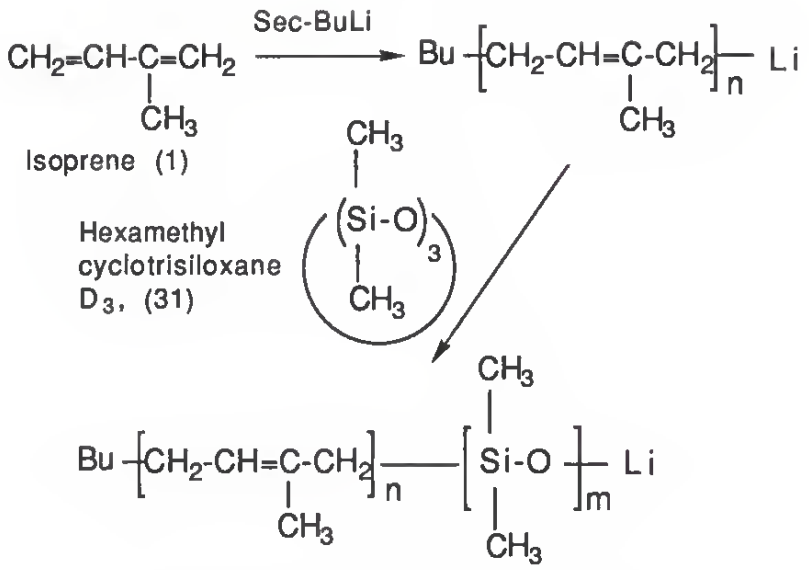



Figure 3.2. Synthesis of poly(butadiene-b-dimethylsiloxane)

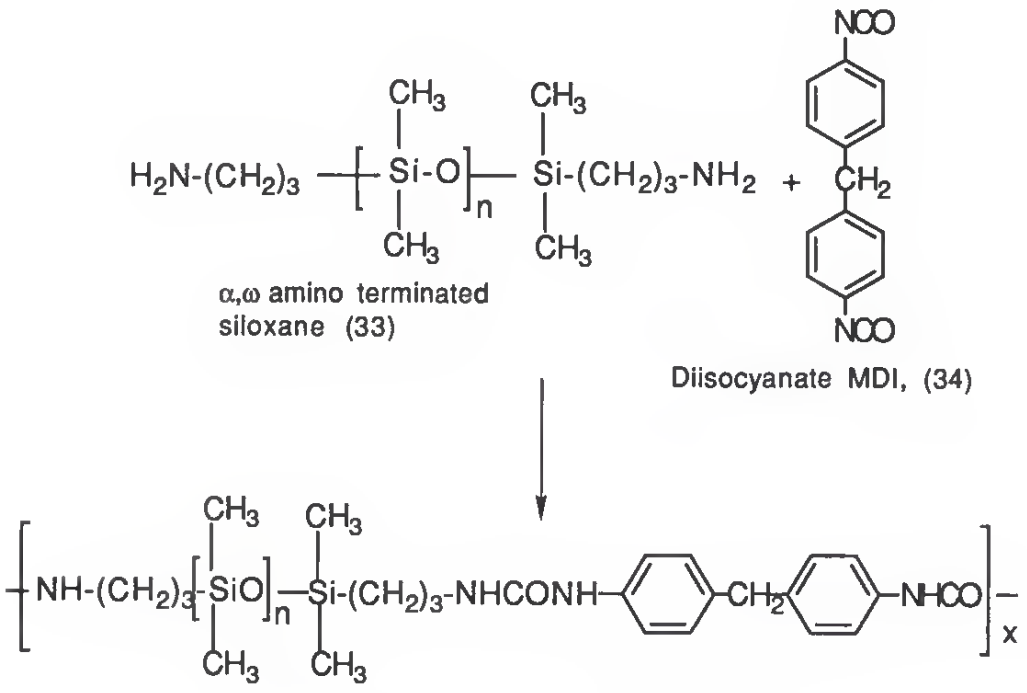



Figure 3.3. Synthesis of siloxane-urethane phase separated copolymer.

Three desirable features ensure the success of these polymerization techniques : 1- The location and concentration of the active sites are known. 2- Contamination by homopolymer is minimal. This results from stoichiometry and purity control in step condensation and from the absence in terminating reactions in living systems. 3- Phase length and sequence are controlled by the order of monomer addition in living polymerization and by a good selection of telechelomer molecular weight in step polymerization.

Living polymerization techniques can be used to produce different types of architectures of the copolymer such as ABA, AB and $(A\text{-}B)_n$. This technique represents one of the best methods to produce regular blocks exhibititng a very low molecular weight distribution. On the other hand, step condensation methods produce broader molecular weight distributions but they are less sensitive to reactive impurities.

Ring opening polymerization, has been frequently applied to the synthesis of siloxane copolymers.[58] Reactive organofunctional terminated siloxane oligomers initiate the polymerization of these cyclic monomers where the functionalities include amino, carboxyl, epoxy, piperazine, chloro and hydroxyl groups. Block copolymers of the ABA type have been synthesized using $\alpha,\omega$-aminopropyl terminated polydimethylsiloxane as an initiator for the ring opening polymerization of N-carboxyanhydrides of several aminoacids, figure 3.4. A PDMS having aminopropyl side chains,[39,81] was employed in the synthesis of graft copolymers.

Teyssie and co-workers[82] used tetraalkylammonium salts of carboxy terminated siloxane oligomers to initiate the ring opening

polymerization of pivalolactone (3,3-dimethyl-2-oxetanone). Pivalolactone is an excellent choice, as the hard phase, because of its high degree of crystallinity. Furthermore its ring strain facilitates ring opening polymerization.

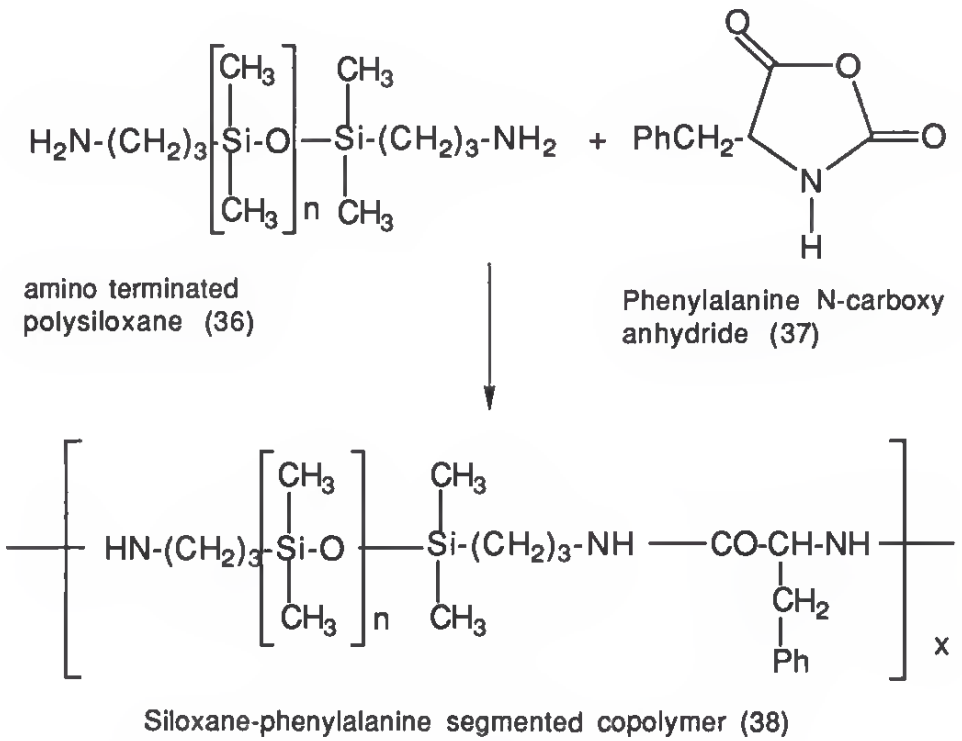

amino terminated polysiloxane (36)
Phenylalanine N-carboxy anhydride (37)
Siloxane-phenylalanine segmented copolymer (38)

Figure 3.4. Synthesis of PDMS-Polypeptide block copolymer.

As mentioned at the beginning of this chapter, two aspects will be considered in the synthesis of siloxane based thermoplastic elastomers: improvement of the thermal stability of the siloxane soft phase and the effect of ring size of the lactone hard phase, in the properties of the graft copolymers. The synthesis of these copolymers is described in the next section.

Synthesis of the Soft Phase in Siloxane Based Multiphase elastomers

Two synthetic schemes were carried out in an attempt to study the influence of the length of the siloxane backbone on the microphase separation of the graft copolymer :

1- Step polymerization from dichlorosilanes.

2- Ring opening polymerization from cyclic monomers plus an end-capper.

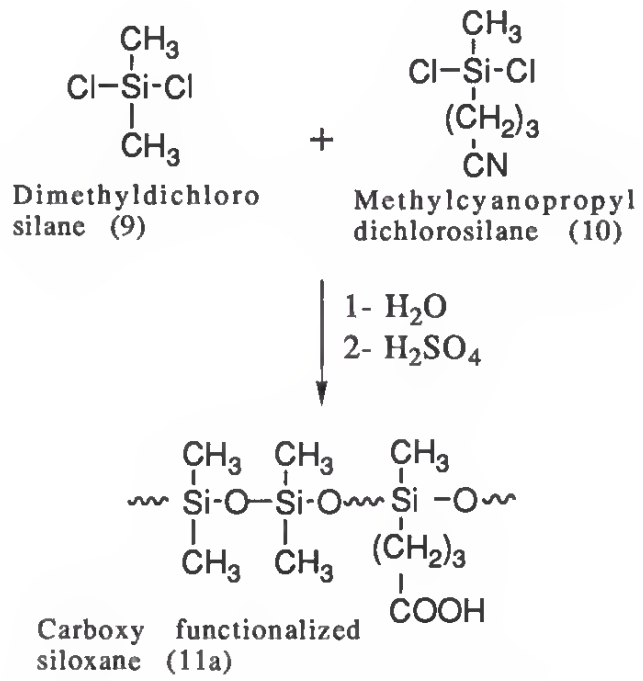



Figure 3.5. Synthesis of polysiloxane with pendant carboxyl groups.

Synthesis of Polysiloxanes from Dichlorosilanes

This method, described by Katayana,[83] consists in the addition of an ether solution of dimethyldichlorosilane (9) and

methylcyanopropyldichlorosilane (10) to an excess amount of water, followed by refluxing of the resulting product with aqueous sulphuric acid in order to hydrolyze the cyano group to the carboxylic acid, figure 3.5.

Progress of the hydrolysis was monitored by IR spectroscopy, figure 3.6, following the slow disappearance of the cyano stretching signal (2240 $cm^{-1}$) and the increasing intensity of the signal for carbonyl stretching (1700 $cm^{-1}$).

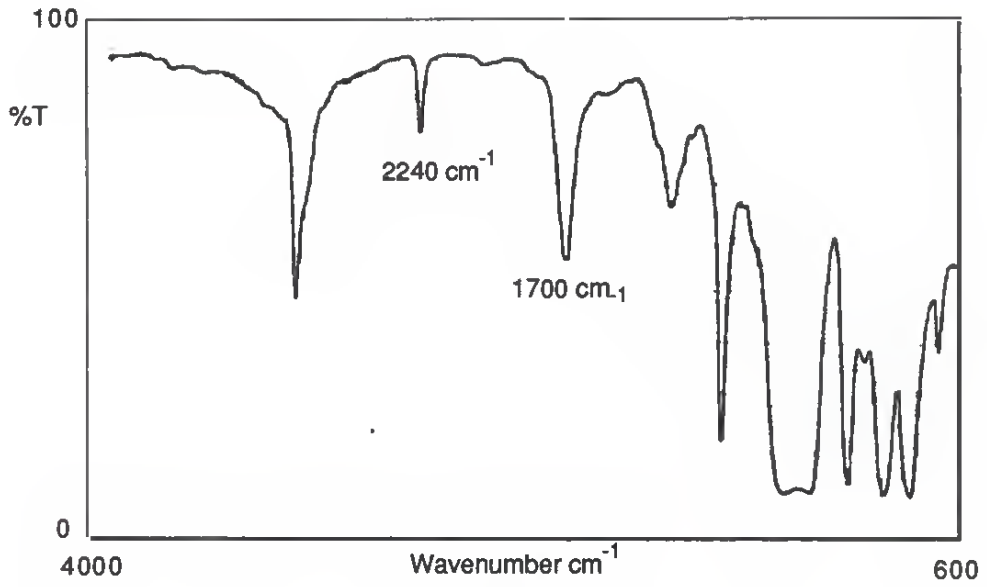



Figure 3.6. IR of polysiloxane

The mixture of the linear polysiloxane (11a) and cyclic oligomers was separated by distillation under reduced pressure and analysis of the volatile fraction by $^1H$ NMR and IR spectroscopy showed that the carboxypropyl functional group was incorporated in the linear polymer. Furthermore, the $^1H$ NMR spectrum of the polymer, figure

3.8, allowed calculation of the number of methylcarboxypropyl units per dimethylsiloxane unit by comparing the relative intensities of the signal at 2.4 ppm ($\underline{CH_2}$-COOH) and the signal at 0.0 ppm ($\underline{CH_3}$-Si), used as reference. This number varied from 27 to 33, smaller than the expected value of 37, as a consequence of the formation of the cyclic oligomers in the reaction.

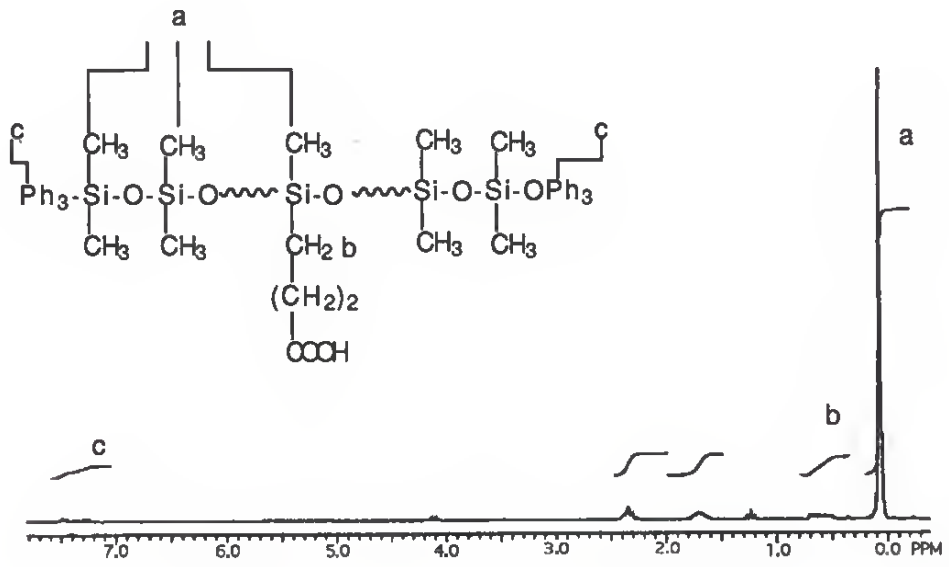



Figure 3.7. $^1$H NMR of polysiloxane.

Synthesis of Polysiloxanes from Cyclic Monomers

This second method of synthesis involved straightforward hydrolysis with aqueous sulfuric acid of a mixture of octamethyl-cyclo-tetrasiloxane ($D_4$) and the corresponding analog with cyanopropyl groups substituting for one of the methyls, figure 3.8. Hexaphenyldisiloxane was added to cap the end groups and minimize scission of the polysiloxane chains by backbiting, as shown in figure

1.17, and to allow molecular weight calculation by $^1H$ NMR end group analysis. In fact the 3 phenyl groups on each side of the chain account for a 30 proton signal as opposed to a 2 proton signal for the hydroxy terminated chains in the non capped polysiloxane. Addition of hexaphenyldisiloxane as a chain terminating agent was somewhat troublesome as most of this compound precipitated out of the reaction mixture (a viscous colorless oil), and its removal required several recrystallizations from ether.

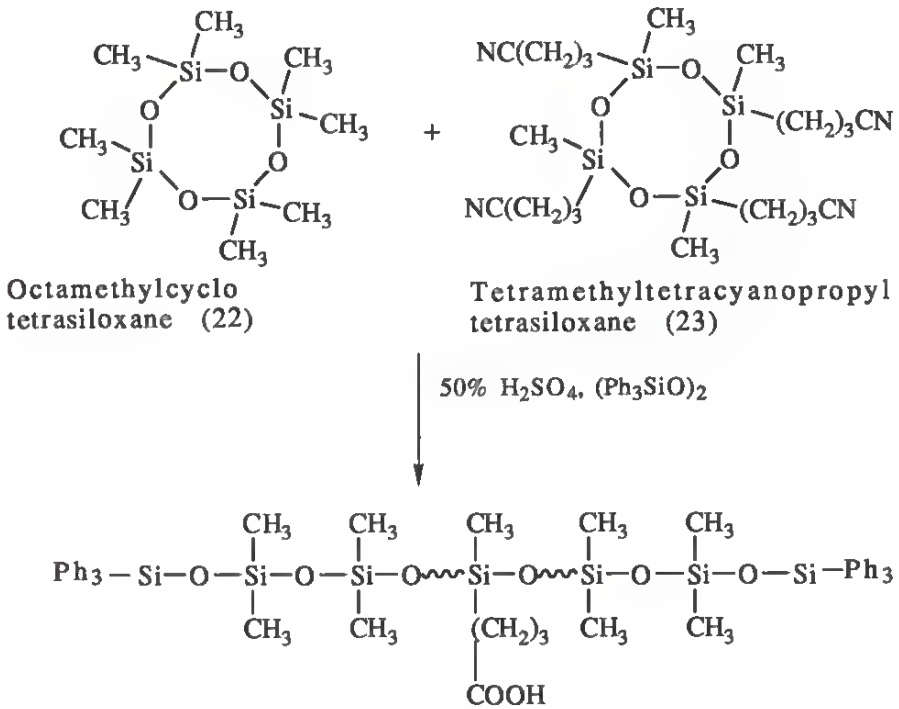



Figure 3.8. Synthesis of end-capped polysiloxane from cyclic monomers.

Molecular weight determination of samples of the polymers obtained by these two different synthetic schemes was undertaken by four different methods:

1- End group analysis.

2- Gel permeation chromatography, GPC.

3- Vapor pressure osmometry, VPO.

4- Viscometry.

The first three methods measure the number average molecular weight, while the fourth measures the viscosity average molecular weight. Considering that these polysiloxanes have been fractionated by distillation under reduce pressure, it can be assumed that the polymer samples consist of a distribution of linear molecules where cyclic oligomers and very low molecular weight linear chains have been eliminated. Molecular weight determined by GPC is relative to polystyrene standards and should be taken just as a reference. It should be noted that it is safe to compare molecular weights of polysiloxanes prepared from dichloro silanes (uncapped) or cyclic monomers (endcapped) only if themolecular weights are determined by the same method. Molecular weights determined by GPC are in the range of 25,000 to 33,000 for both products, suggesting that the endcapping reaction did not occur efficiently, an observation anticipated by the precipitation of the endcapper from the reaction mixture. A more realistic figure of Mn = 5000 was obtained by VPO, since the method was independently checked by determining the molecular weight of a polystyrene standard $M_n$ =12,000, obtaining a measurement of 10,800.

The synthetic scheme is continued by treating the polymer containing carboxyl pendant groups (11a) with a concentrated solution of KOH for a short time (only five minutes to avoid degradation), and the result is the corresponding salt (11b), figure

3.9. Formation of the salt was confirmed by IR, and by increase in water solubility which led to emulsions when the product was extracted with diethylether. This carboxylate salt is used as the initiator for the ring opening polymerization of lactones.

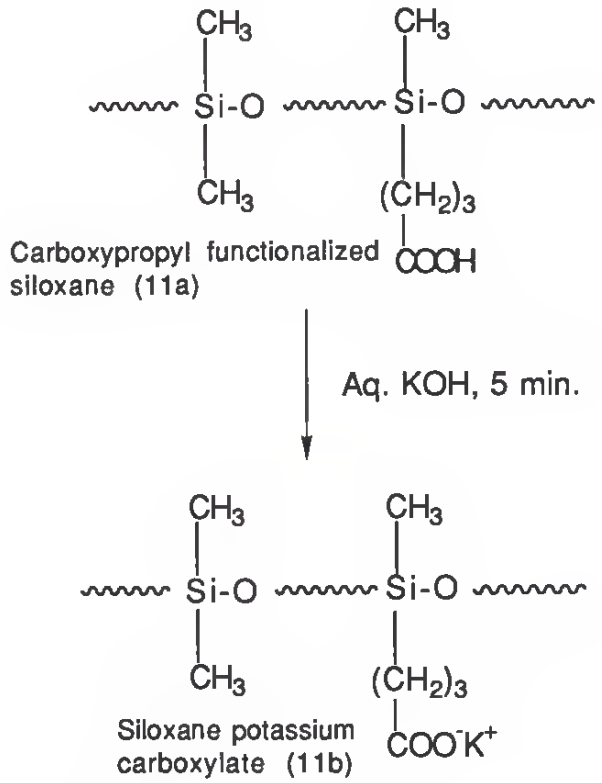



Figure 3.9. Formation of the polysiloxane potassium carboxylate.

## Ring Opening Polymerization of Lactones

### Polymerization of Pivalolactone

Pivalolactone reacts with nucleophiles at two sites, figure 3.10. Strong nucleophiles attack the carbonyl group[84,85] while weak

nucleophiles attack at the methylene carbon.[86] Lenz,[55] Hall,[56] and Beaman[57] studied the polymerization of pivalolactone and found that

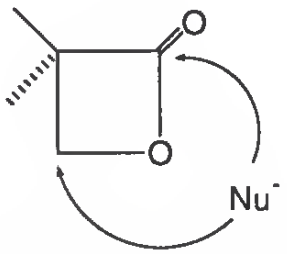



Figure 3.10. Two sites of attack at pivalolactone.

the less nucleophilic carboxylate anion polymerized pivalolactone smoothly, opening the ring with alkyl oxygen cleavage to form a carboxylate propagating species. Polymerization of pivalolactone with carboxylates affords living polymers, and no termination or chain transfer occurs. This process requires the absence of water; therefore, drying of the carboxylate is essential.

Synthesis of poly(siloxane-g-pivalolactone), figure 1.15, was carried out in tetrahydrofuran, THF, using the potassium salt of the carboxyl functionalized siloxane (11b) as the initiator.[59] The reaction became heterogeneous in five minutes, yet the polymerization continued, and a 24 hr period was sufficient to produce monomer conversions greater than 90%. Heterogeneous graft copolymerizations of this nature are rare, and in this case the reaction could be done only in the presence of 18-crown-6. This crown ether is known to complex with the potassium counterion rendering the carboxylate anion an efficient initiator for lactone polymerization. Control experiments showed that the crown ether

by itself did not polymerize pivalolactone, nor did hydroxy terminated polysiloxanes. This indicates that hydroxy groups are much slower initiators than carboxylate anions. Copolymers with compositions ranging from 10 to 90 weight % pivalolactone were obtained; DSC analysis showed excellent microphase separation of the hard phase (pivalolactone) and soft phase (siloxane), while contact angle studies indicated a surface rich in siloxane.[59]

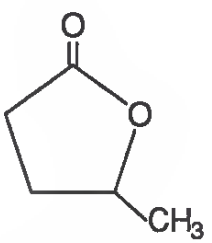
A variation in this synthetic procedure, substitution of KH in THF for aqueous KOH in figure 3.9, was attempted in order to obtain the siloxane carboxylate, (11b). This approach simplifies the overall procedure, as the THF solution of the carboxylate is carried directly on to the next step, addition of pivalolactone monomer, thus avoiding the time consuming extraction, purification and drying of the carboxylate. Synthesis of copolymers with 30 and 50 weight % pivalolactone was attempted; however, homopivalolactone was obtained in most cases, and mixtures of the homopolymer and the copolymers in the rest. The cause of the homopolymerization of pivalolactone may well be the presence of an excess of KH besides extraneous moisture in the solvent, which would generate potassium hydroxide, also would produce homopolymer.

Following the method reported before,[59] poly(siloxane-g-pivalolactone)s containing 30 and 70 weight % pivalolactone were synthesized, and these polymers afforded free standing films from 10 % solutions in hexafluoroisopropanol, HFIP. Film formation is indicative of high molecular weight which is responsible for the unique properties of the polymer.

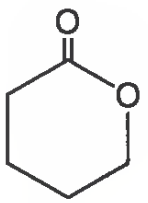
High molecular weight, together with a narrow molecular weight distribution, assured by the living nature of the synthetic technique and the high percent crystallinity of polypivalolactone, contribute to the achievement of excellent phase separation in the copolymer.

Polymerization of Other Lactones

The polymerization of the five and six membered lactones, γ and δ valerolactone, figure 3.11, was attempted in order to study the effect of the ring size on the properties of the graft copolymer.




γ-valerolactone (39)




δ-valerolactone (40)

Figure 3.11. Structures of γ and δ valerolactones.

Carothers found that while six membered ring lactones polymerized, five membered ring lactones did not.[63] This was confirmed by Hall and Schneider,[87,88] who systematized the information on the polymerization of cyclic esters, urethanes, ureas, imides and amides, and added their own contribution to supply a wealth of information on this field.

In our hands the ring opening polymerization of δ-valerolactone by the carboxylate functionalized siloxane proceeded in the presence of 18-crown-6 in THF at 90°C, figure 3.12. A soluble graft copolymer was obtained, as confirmed by GPC, where the siloxane (11b) molecular weight was calculated as 5000 while the copolymer showed a single signal, molecular weight 15000. A temperature much higher than that required for the polymerization of pivalolactone (room temperature) was necessary for the polymerization of δ-valerolactone since the latter contains less ring strain. On the other hand, γ-valerolactone did not polymerize, regardless of the experimental conditions employed.

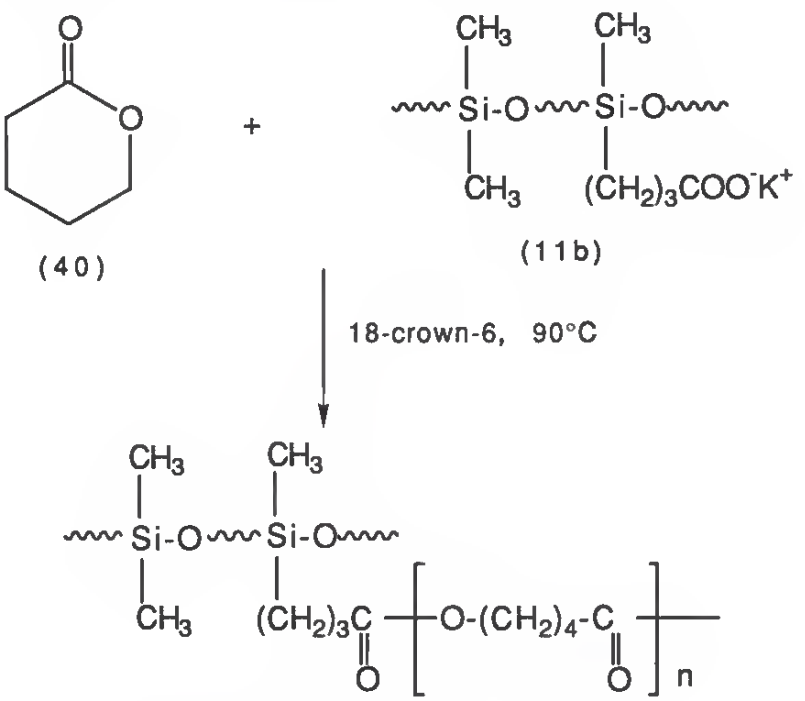



Figure 3.12. Synthesis of poly(siloxane-g-δ-valerolactone).

In conclusion the ring strain of the lactone is directly related to its polymerizability and to the conditions under which polymerization occurs. The polymerization required the presence of 18-crown-6 to increase the nucleophilicity of the carboxylate anion by trapping the potassium counterion. While the siloxane-pivalolactone graft copolymer (12) was insoluble in most organic solvents, the siloxane-δ-valerolactone counterpart (41) was easily soluble in organic solvents due to its relatively low molecular weight, 15,000 (GPC).

Improving the solvent resistance of siloxane based multiphase polymers has been one of the goals of this dissertation. With this in mind, other cyclic compounds such as lactams were considered as hard phases. This chemistry is discussed in the next chapter.

# CHAPTER 4
# SILOXANE-LACTAM GRAFT COPOLYMERS

The synthesis of siloxane-lactone graft copolymers was discussed in the previous chapter, where the combination of soft and hard phases produced film forming thermoplastic elastomers. A similar approach will be described in this chapter, substituting lactams for lactones.

While siloxane-polyamide block and segmented copolymers have been studied before,[89,90] little is known about siloxane-polyamide graft copolymers. Polyamides are mechanically very strong and have a wide range of applications in industry. The combination of siloxanes and polyamides could lead to other desirable properties such as enhanced impact resistance, excellent solvent resistance, elastomeric behavior and altered surface properties.

Amide linkages have cohesive energies (8.5 kcal/mole) that are intermediate between ureas (14.3 kcal/mole) and imides (4-6 kcal/mole). Although polyurethanes produce stronger intermolecular hydrogen bonding than polyamides, polyurethanes are thermally unstable. Therefore when hydrogen bonding and thermally stable polyamides are combined with elastomeric low Tg siloxanes, novel elastomers with improved solvent resistance and good thermal stability might be obtained.

## Polyamides

Polyamides are produced by the reaction of diamines with dicarboxylic acids in which the linkage forming the main chain of the macromolecule occurs through the formation of amide bonds.

### Nylon 6 and Nylon 66

The generic term "nylon" has been adopted by the U.S. Federal Trade Commission for designating fibers of the polyamide type.[91] The common nomenclature uses the word nylon, followed by numbers designating the number of carbons constituting the repeat unit of the polymer; for example, the reaction between hexamethylene diamine (42) and adipic acid (43) produces nylon 66 (44), figure 4.1,

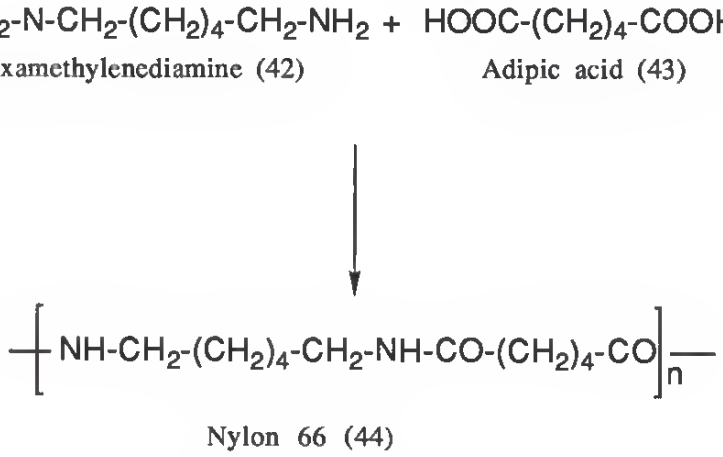
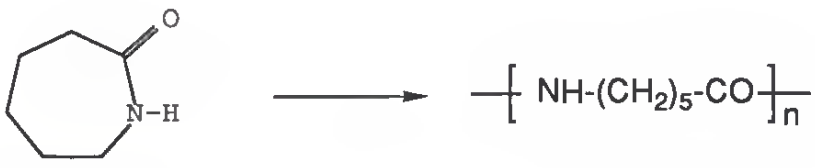



Figure 4.1. Synthesis of nylon 66.

while the polyamide from caprolactam (45), which contains 6 carbon atoms, is known as nylon 6, (46) figure 4.2. Polyamides, together with polyester and polyacrylonitrile, constitute the most important group of polymers in the production of textile fibers.[91]




Caprolactam (45) Nylon 6 (46)

Figure 4.2. Synthesis of nylon 6.

The first polyamide was synthesized by Gabriel and Maas in 1899.[92] They observed that upon heating ε-caprolactam a very tough material was produced; however, they did not realize the importance of their observation. The synthesis and development of nylon as the first synthetic fiber was the product of the genius of Wallace Hume Carothers and the observation of his chief associate Julian Hill. Carothers, then a professor at Harvard University, was attracted to E. I. du Pont de Nemours & Co. in 1928, where he was allowed to conduct fundamental research, *without regard for any inmmediate commercial objective.*[93] Du Pont had become involved in the production of cellulose acetate fibers in 1929, and it is a credit to the vision of its management that Carothers was allowed complete freedom in his work and given all the resources he requested, which in the end led not only to nylon but to neoprene and to macrocyclic compounds such as the synthetic musks.[93]

Carothers' initial interest was only general polymer research. For some time he had been mentally exploring the possibility of imitating nature in the creation of "giant" molecules such as cotton, silk and wool.[94] He reasoned that just as ethyl alcohol and acetic acid will react with each other to form ethyl acetate so, in a similar way, would a dialcohol react with a diacid, leading to a product with reactive ends that could further react in the same manner to produce a compound with a longer carbon backbone, as shown in figure 4.3.

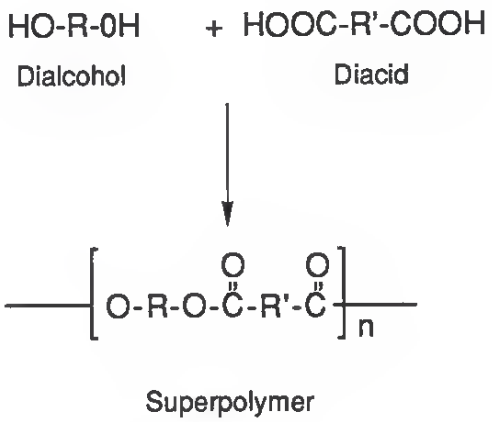



Figure 4.3. Synthesis of Carothers superpolymer.

Nylon Fibers

The need for difunctional starting materials is one of the fundamental principles of step polymerization. By applying this method and using a molecular still, Carothers assistant Julian Hill observed that the compounds he had been working with had displayed profound changes. The new material was tough and elastic and more importantly, fibers were formed when a glass rod was dipped into

the material and lifted. Carothers called these materials *superpolymers*. It was suggested that the discovery might be useful as a textile fiber; however, the product had low melting point, was soluble in hot water and in common cleansing fluids.

Carothers turned his attention to polyamides, prepared a wide range of diamines, from $C_2$ to $C_{18}$, evaluated them as monomers and reacted them with a variety of aliphatic diacids to produce the corresponding polyamides.[63] More than 100 *superpolymers* were prepared which produced fibers that resisted heat, washing and dry cleaning. This new group of synthetic materials was given the generic name nylon. Nylon was the first purely synthetic fiber, and newspapers announced its discovery as one of the most important in the century.[94]

Following publication in the early 1930s of Carothers research on polyamides and polyesters, Schlack[95] in 1937, synthesized nylon 6 from ε-caprolactam using ε-aminocaproic acid as catalyst, at I.G. Farbenindustrie. The I.G. Farben group succeeded in commercially producing nylon 6 monofilaments under the trade name of Perluran™ in 1939. Du Pont produced nylon 66 fine denier fibers for experimental evaluation in April 1937,[96] its first commercial plant for the production of nylon 66 began operations in December 1939. In May 1940, fine denier nylon was available nationwide.[97] It is a tribute to the vision of the earlier developers such as Carothers and Schlack that still today nylon 6 and nylon 66 represent the largest volume of total polyamides converted to fibers.

In 1932 Carothers and Hill[98] stated the requirements for fiber forming polymers as follows: 1- The polymer must consist of very

large molecules having a number average molecular weight of not less than 12,000 and a molecular chain length of not less than 1000 Å. 2- The polymer must be capable of crystallizing. 3- Three dimensional polymers such as cross-linked polyamides and polyesters are generally unsuitable.

These requirements have remained relatively unchanged despite the large amount of research that has followed the original work. Since small molecules and polymer molecules with molecular weights below a critical value (called the molecular weight for entanglement) are weak and readily attacked by solvents and other reactants, it is apparent that the unique properties of polymers are related to molecular weight. Thus toughness, impact strength, melt viscosity, modulus, tensile strength, thermal stability and resistance to corrosives are dependent on molecular weight and molecular weight distribution. However, while a molecular weight above the critical value is essential for most practical applications, extremely high molecular weight polymers are very expensive to process.

The critical value for molecular weight depends on Tg, the cohesive energy density for amorphous polymers and the degree of crystallinity for crystalline polymers. The degree of crystallinity depends on the molecular constitution and stereoregularity of the chains. With the exception of polymers with high stereoregularity, such as isotactic polypropylene, strong intermolecular forces such as hydrogen bonding are required for fibers. Thus, while a molecular weight of 12,000-15,000 is sufficient for a commercially useful

polyamide fiber, molecular weights of the order of $10^6$ are necessary for polyethylene body implants.

It is important to note that in 1945 it was reported that Farbenindustrie had evaluated more than 3,000 polyamide constituents without finding any commercially feasible polyamides with important improvements over nylon 6 and nylon 6,6. At the same time research on this field was being carried out at Du Pont and several other companies.[93]

## Polymerizability of Lactams

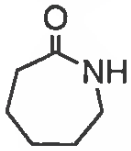
While at du Pont Hall put together the existing information on the polymerizability of lactams[88] and contributed his own share to this field. With the information gathered he made some generalizations: (a) "Water and sodium hydride were equally effective catalysts at temperatures above 200 °C. At room temperature water was ineffective but sodium hydride was still potent". (b) "Ring opening polymerization of lactams was a restricted technique, with the majority of lactams failing to polymerize". (c) "Of the five 8- and 9-membered ring lactams examined all polymerized. Approximately one half of the various 7-membered ring compounds studied to that date (1958) polymerized. Most six membered ring lactams did not polymerize." (d) "Aryl and alkyl substituents on a ring decrease polymerizability, especially if they are on the nitrogen atom of the lactam".

These statements have been revised as a consequence of the vast amount of work performed on this field in the following years. For example, water and sodium hydride are not catalysts but

initiators of the reaction and their mode of action is very different. Polymerization of lactams can be initiated not only by water and bases but also by acids.[99-102] Water initiated polyamidation is the method most frequently used in industry followed by anionic polymerization, while cationic initiation is not useful because the molecular weights of the polymers that result are not sufficiently high. Nylon 6 is the material of major importance in commercial production, while nylon 12 and nylon 8 are of lesser importance.

Hydrolytic polymerization of caprolactam is carried out commercially in batch and continuous processes by heating the monomer in the presence of 5-10% water to temperatures of 250-270°C. Three equilibria have been proposed for the water initiated polymerization of lactams :

1-Hydrolysis of the lactam to the amino acid;

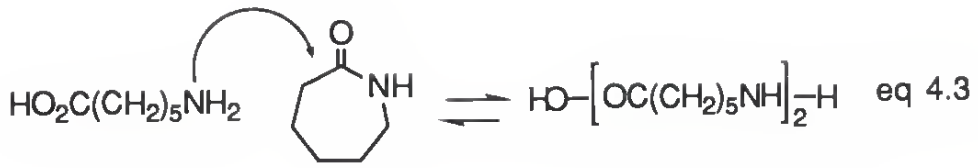



$$+ H_2O \rightleftharpoons HO_2C(CH_2)_5NH_2 \qquad \text{eq 4.1}$$

2-Step polymerization of the amino acid with itself;

$$2\ HO_2C(CH_2)_5NH_2 \rightleftharpoons \sim\sim CO\text{-}NH \sim\sim + H_2O \qquad \text{eq 4.2}$$

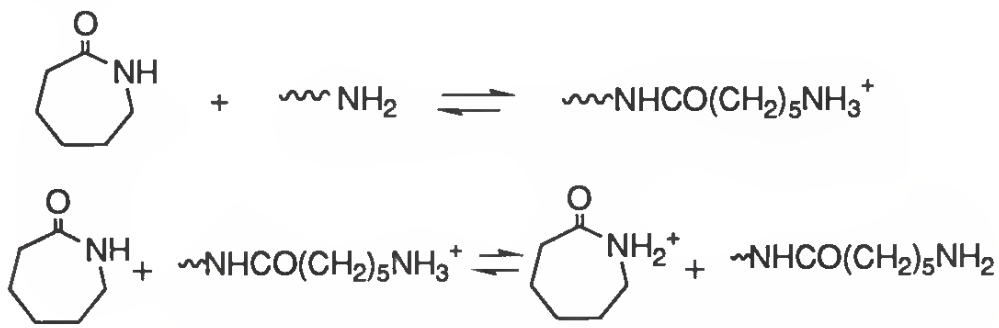
3-Ring opening polymerization of the lactam by the amine group of the amino acid;




eq 4.3

followed by propagation in the same way as reaction 4.3.

Ring opening polymerization is the most likely route, while step polymerization of the amino acid with itself accounts only for a very low percentage of the reaction. Polymerization is acid catalyzed as indicated by the fact that amines or $NH_2(CH_2)_5COONa$ are poor initiators in the absence of water. Therefore initiation and propagation are believed to occur by the following sequence :




On the other hand, anionic polymerization of lactams occurs via the lactam anion which reacts with another molecule of monomer by ring opening transamidation.[99-102]

A series of new lactams have been synthesized and, in most cases, successfully converted into the corresponding polymers. The traditional hypothesis that five and six membered lactams are very stable and therefore unpolymerizable has been revaluated. Even substituted rings which until recently were considered unpolymerizable successfully incorporated as linear units into

polymer or copolymers.[109] Most of these lactams have been polymerized under anionic conditions, which require the use of dry solvents, and solubility of the forming polymer becomes the factor controlling its molecular weight. As mentioned earlier, most industrial processes for the production of nylon 6 use water as initiator.

Bearing in mind that the main goal of this dissertation is the synthesis of thermoplastic elastomers using the soft-phase, hard-phase approach, ε-caprolactam was chosen as the monomer to graft onto the functionalized siloxane, because of polycaprolactam (nylon 6) high crystallinity, high melting temperature and commercial availability. According to M.I. Kohan,[104] nylon was a new concept in plastics for several reasons. It was crystalline which meant a sharp transition from solid to melt and it meant higher service temperatures. A combination of toughness, rigidity and "lubrication free" performance, peculiarly suited it to mechanical bearing and gear applications. Nylon acquired the reputation of a quality material by showing that a thermoplastic could be tough as well as stiff and do jobs better than metals in some cases. This performance gave nylon the label "an engineering thermoplastic".

## Polysiloxane-Lactam Graft Copolymers

Polymerization of caprolactam was carried out in two steps: 1-the monomer was mixed in a thick reaction tube with catalytic amounts of water, frozen, evacuated and sealed. The reaction mixture was then heated to 250-260°C for several hours; 2- the tube was cooled opened and heated again at 180°C to distill the

water as well as to increase the molecular weight of the polymer.[105]

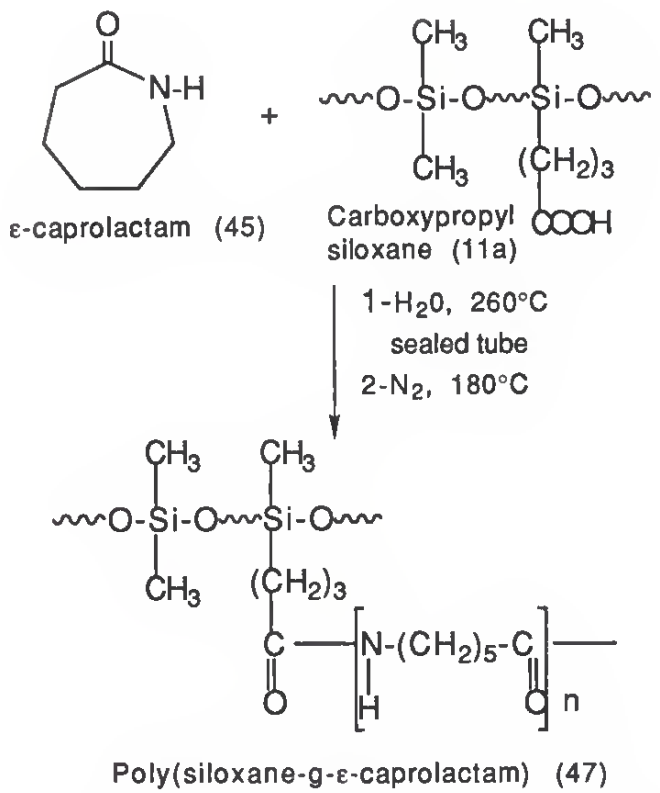



Figure 4.4. Synthesis of poly(siloxane-g-ε-caprolactam)

The chemistry was conducted combining a one to one mixture (W/W) of caprolactam and functionalized siloxane. The final product was extracted with dichloromethane, ether and acetone to eliminate any unreacted mixture, then dissolved in m-cresol and recrystallized by adding diethylether. The purified polymer was dissolved in hexafluoro isopropanol (2 % by weight) and free standing films were easily produced by pouring the solution in a Petri dish and letting the solvent evaporate. Formation of free standing films is a

condition "sine qua non" for the potential use of a polymer as thermoplastic elastomer or engineering material. Only high molecular weight polymers fulfill this condition as the intermolecular interactions, through hydrogen bonding of the amide groups, must overcome intramolecular forces and entropy driven random coils and thus induce crystallization.

Characterization of Poly(siloxane-g-ε-caprolactam)

The siloxane-lactam copolymer was analyzed by $^{1}H$ NMR, $^{13}C$ NMR, IR, XPS and water contact angle techniques. The $^{1}H$ NMR spectrum, figure 4.5, allowed analysis of siloxane-lactam ratios.

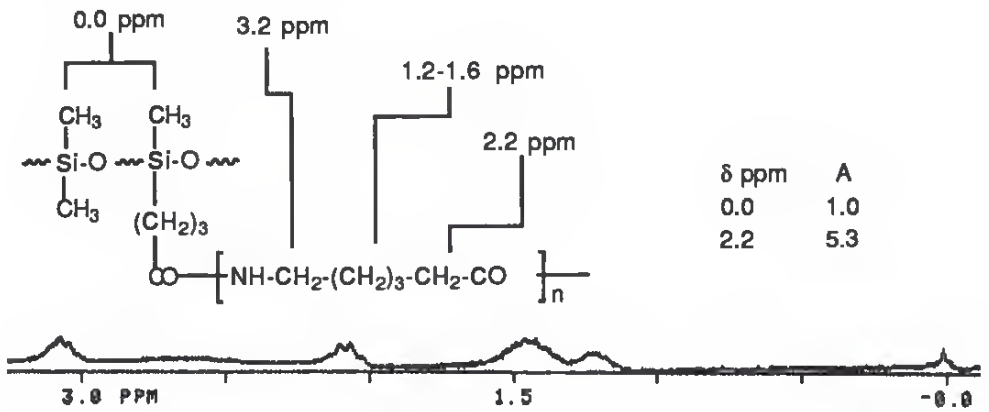



Figure 4.5. $^{1}H$ NMR of poly(siloxane-g-ε-caprolactam) 4/96 W%

By comparing the integration of the signals at δ = 0.00 ppm ( $CH_3$-Si ) and δ = 2.2 ppm ( $CH_2$-CO ), a siloxane content, in weight %, of 1.7-4.0 % was calculated. Although the weight % of both monomers was initially the same, in all reactions, most of the siloxane was recovered by extraction with ether, dichloromethane or

acetone. Carbon NMR, figure 4.6, which is less sensitive than proton NMR, did not show signals for the $CH_3$-Si groups due to the low siloxane content in the copolymer, while the signal for the C=O of the lactam segment (178.4 ppm) was noticeably intense. It also showed individual signals for the other five lactam carbons.

IR of copolymer films, figure 4.7, showed the characteristic signals of polyamides ($cm^{-1}$) : 3250, 3050, N-H stretching of polymeric amides,[106] 1625 and 1530, amide bands 1 and 2, corresponding to C=O stretching and 1070, Si-O stretching.

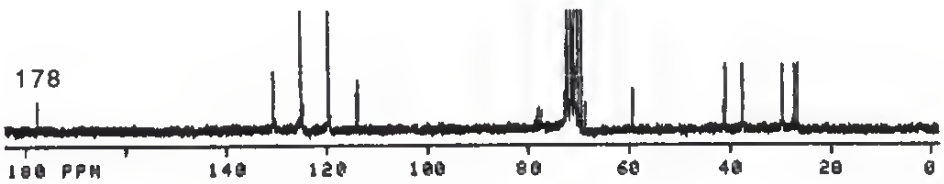



Figure 4.6. $^{13}C$ NMR of poly(siloxane-g-ε-lactam) 4/96 w%.

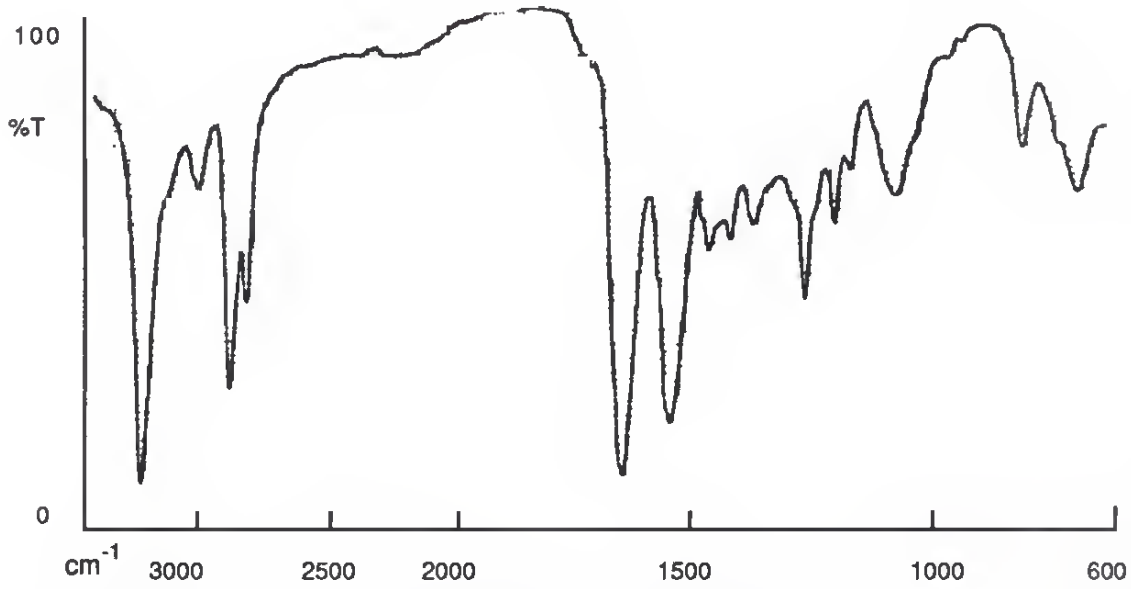



Figure 4.7. IR of poly(siloxane-g-ε-caprolactam).

Surface analysis of the films by XPS, figure 4.8, shows a 61.1/18.3, C/Si ratio which indicates a surface rich in siloxane when compared to 50/25 for PDMS and 74.6/0.6 for a copolymer where both the siloxane and lactam segment shared the surface. This siloxane rich surface should be hydrophobic, as confirmed by the water contact angle = 90.5° measured on the copolymer films.

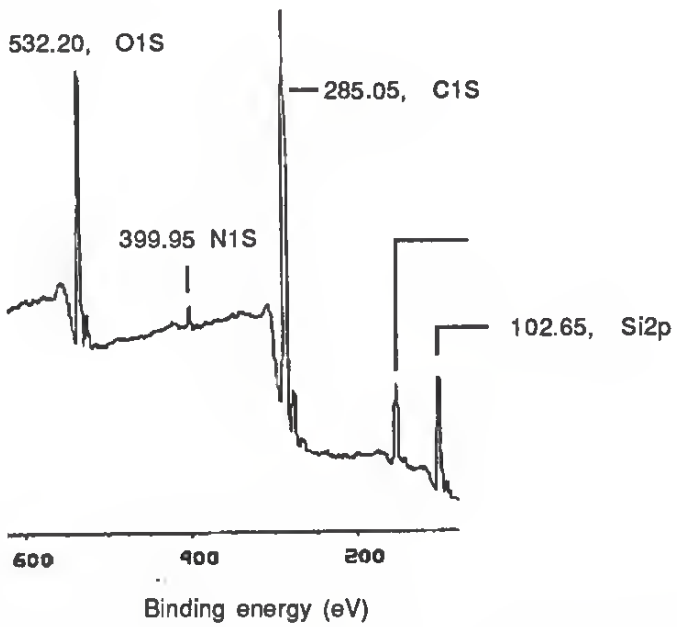



Figure 4.8. XPS of poly(siloxane-g-ε-caprolactam).

Phase segregation of the siloxane and the lactam components is also observed by optical microscopy using 90° polarized light; a picture of a film of poly(siloxane-g-ε-caprolactam) is shown in figure 4.9. The crystalline phase, show birefringence and appears as a white solid while the amorphous phase constitute the black background in the picture.

Copolymers like the one mentioned above are interesting as a surface modified nylon, and could be of commercial importance. Nylon is a hygroscopic material and this is one of the main causes for its deterioration upon long exposures, specially in very humid environments. Given the commercial importance of nylon, extensive research has been dedicated to its surface modification. Siloxanes and highly fluorinated polymers are most frequently used as surface modifiers. Due to their large molar volumes, low cohesive energy densitities and high flexibility (low Tg), polydimethylsiloxanes have low surface tension and surface energies.[107] The surface tension for high molecular weight PDMS 21-22 dynes/cm is at least 10 dynes/cm lower than that of many other polymers such as polystyrene (30-34 dynes/cm), poly(ethylene terephthalate) (40-43 dynes/cm), and nylon (38-42 dynes/cm).[107] Most polymers interfacial surface tensions are below 10 dynes/cm, and as a result the air-polymer surfaces of siloxane containing copolymers as well as their blends are enriched in the lower surface energy siloxane.[108] Properties which can be improved by surface modification with siloxane are biocompatibility, hydrophobicity, surface finish and gloss, release properties, reduction in friction and atomic oxygen resistance.

Siloxane segmented, block and graft copolymers have been shown to be very useful in polymer surface modification through blending.[109] The organic component of the siloxane can be chosen to be similar with the base polymer in order to achieve compatibility. Siloxane homopolymers are usually incompatible with the base polymer and thus may eventually separate from the material surface.

As opposed to blends, the siloxane phase in siloxane copolymers is chemically bonded to the organic counterpart therefore macrophase separation is not a problem.

Until recently surface modification of nylon through siloxane graft copolymers has been elusive. However the successful synthesis of surface modified nylon as described herein has been acomplished through the grafting of caprolactam to polysiloxane with carboxyl pendant groups, as confirmed by XPS and water contact angle measurements.

Since our original goal was to synthesize thermoplastic elastomers, it is important to be able to produce a copolymer with higher percentage of siloxane to introduce the necessary elasticity. The initial method used to prepare the copolymer yielded products with up to 4 % siloxane.

In an attempt to increase the incorporation of siloxane in the copolymer (47) the initial reaction mixture was dissolved in toluene and refluxed for several hours at 120°C, then the temperature was increased to distill the solvent to a maximum of 250°C. The product was purified as before and characterized by IR, $^{1}H$ NMR and $^{13}C$ NMR. Although the copolymer (47) contained 18 % by weight of the siloxane segment, calculated by $^{1}H$ NMR, figure 4.10, it did not, produce free standing films. Calculation of the chain length of the lactam segment for this copolymer revealed 111 repeat units while the one containing 4 % siloxane, corresponds to 695 repeat units. This is equivalent to molecular weights of 12,500 and 78,000 respectively.

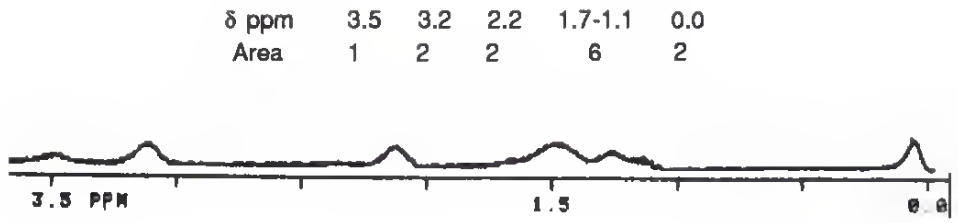



Figure 4.10. $^{1}H$ NMR of poly(siloxane-g-ε-caprolactam) 18/82 w%.

In contrast to the copolymer containing 4 % siloxane, the $^{13}C$ NMR of the copolymer containing 18 % siloxane, figure 4.11, showed a signal for the $CH_3$-Si while the signal for the C=O was very small.

It may well be that in the initial step in the reaction using toluene the lactam/linear poyamide equilibrium leans towards the lactam in a higher percent than in melt reactions, and consequently the molecular weight of the graft is decreased. The final product in the commercial production of nylon 6, contains 8-9% of caprolactam as well as 3% of cyclic oligomers.[101]

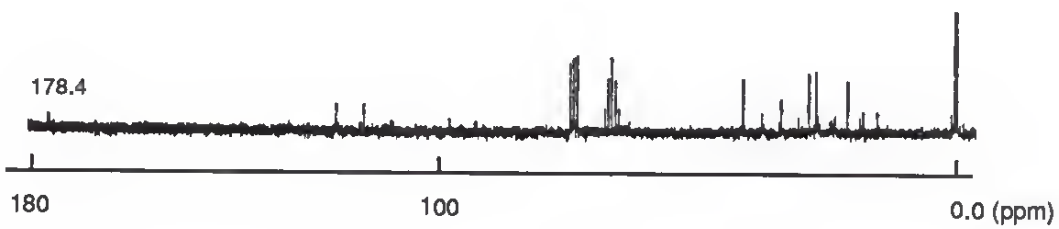



Figure 4.11. $^{13}C$ NMR of poly(siloxane-g-ε-caprolactam) 18/82 w%.

## Conclusions

Reaction of ε-caprolactam with carboxy functionalized siloxanes, in the melt, afforded film forming polysiloxane-nylon graft copolymers with 1.7-4.0% siloxane. These copolymers show excellent phase segregation as indicated by surface analysis (XPS and water contact angle measurements).

Similar reactions carried out under dilute conditions provided graft copolymers with a higher siloxane content (18%) however, the molecular weight of the nylon segment was not high enough to induce formation of free standing films. Most likely these dilute conditions favored the formation of cyclic products over high molecular weight linear poycaprolactam chains. The film forming poly(siloxane-g-ε-caprolactam) could be of commercial use as a *self lubricating* nylon.

# CHAPTER 5
# EXPERIMENTAL

## Instrumentation

All NMR spectra were obtained on a Varian XL-200 spectrometer using deuterated chloroform as solvent and TMS as reference; chemical shifts reported in ppm. For polymers containing siloxanes, no TMS was used, the methyl signal of the methyl siloxane was used as reference instead. IR spectra were recorded on a Perkin Elmer FT spectrophotometer or a Perkin Elmer 281. GC was performed on a Hewlett Packard 5880A series gas chromatograph, equipped with a FID detector and a fused silica 0.31mmx50m capillary column packed with a 0.17m film of SE-54 (methyl-phenylsilicone), HPLC on a liquid chromatograph with the following conformation: U6K injector, a Waters 590 pump, a variable wavelength UV-VIS Spectroflow 757 detector and a Waters Novapak C18 column 150x3.9mm. GPC was carried out on a liquid chromatograph equipped with a Waters M6000A pump, a concentration sensitive differential refractometer and two attached Phenogel columns (300x 7.8 mm, cross-linked polystyrene-divinylbenzene, 500 and 50000Å), all data was collected and analyzed on a Zenith personal computer model 48 equipped with a Metrabyte multi-IO card and an Epson dot matrix printer. VPO was performed on a Wescan 233 molecular weight

apparatus, XPS on a Kratos XSSAM 800instrument with Mg anode at 12 KV, 19 mAmp, $3x10^{-8}$ Torr, software DS800.

## Chemicals

All solvents were reagent grade, THF was refluxed overnight over a sodium and potassium alloy (2:1) and distilled under argon before use. The argon was purchased from Air Products and dried by passing it through sulfuric acid, concentrated sodium hydroxide and calcium sulfate. Pivalic acid (PVA), 2-(2-methoxyethoxy)ethanol (MEEtOH), DMAP, DCC, were purchased from Aldrich and vacuum dried before use and titanium tetrabutoxide from Fisher Scientific.

D,L-alanine (Eastman Kodak) was recrystallized from water, Vacuum sublimed and stored in a desiccator containing calcium sulfate.

Chlorosilanes, cyclic siloxanes , hexaphenyl disiloxane, were purchased from Petrarch (Huls America) and stored in a refrigerator. One gallon of dimethyl,dichlorosilane was donated by Dr Paul Kremer of PCR Inc at Gainesville. Pivalolactone was donated by Dr Gus Ibay of Southern Research Institute; δ-valerolactone and γ-valerolactone were purchased from Aldrich. All lactones were processed before use by stirring them overnight with cacium hydride and distilling under reduced pressure.

E-caprolactam, (gold label, Aldrich) was recrystallized from cyclohexane, dried in a vacuum oven at 40°C for 10 hrs and stored in a desiccator containing calcium sulfate.

## Esterification of Pivalic Acid. Model Studies

### Synthesis of 2-(2-Methoxyethoxy)ethyl Pivalate(29)

A solution of pivalic acid (27) (3.9 nmol), MEEtOH (28)(5.0 mmol), DMAP (0.53 mmol), DCC (3.8 mmol), in diethylether (25 cc) was left stirring under argon at RT for 15 hrs. The N,N-dicyclohexyl urea formed was filtered and the filtrate washed with water (3x25 cc), 5% acetic acid (3x25 cc) and dried with magnesium sulfate. The crude product was recovered after evaporation of the ether under reduced pressure, purified by CC ($Al_2O_3$, hexane-dichloromethane gradient) and characterized as follows:

White solid, m.p.: 178-9°C.

IR (film, $cm^{-1}$): 2890(s), C-H str.; 1725(m), C=O str.; 1120(s), C-O str.

$^1H$ NMR (δ,ppm): 1.95,s,3H; 1.30,s,3H; 1.32,s,3H, corresponding to pivalic acid methyl groups; 3.9,s,3H, $O\underline{C}H_3$, 3.5-3.75,m,6H, corresponding to the internal methylene groups of the ester; 4.25 ,t, ( j=7Hz), 2H, $COO\underline{C}H_2$.

$^{13}C$ NMR (δ,ppm): 27.02 $(\underline{C}H_3)_3C$; 38.59 $(CH_3)_3\underline{C}$; 58.81, $O\underline{C}H_3$; 61.44,$COO\underline{C}H_2$; 178.3 $\underline{C}$=O.

M. Sp. (m/e, %I): 204, 21,$M^+$; 173, 0.29, loss $OCH_3$; 129, 100, loss OCH2CH2OCH3, 103, 19.7 pivalate cation; 85, 14, pivalate minus $CH_3$; 57, 42, (CH3)3C+.

Esterification Reactions.

These reactions were carried out in 50 cc 3 necked flasks with a thermometer in one neck, a rubber septum in the other and a condenser in the center, connected to a Schlenk line (argon, vacuum). Equimolar amounts of pivalic acid (27) and MEEtOH (29) were dried separatly under vacuum, overnight, then mixed together under argon and magnetic stirring. Two different ways of removing the water formed in the reaction were employed: 1- Vacuum, at room temperature. 2- A stream of argon and heating to the refluxing temperature of the mixture, 160°C at the begining and 190°C at the end. Samples (0.05-0.10 cc) were syringed out through the septum with argon filled syringes and analyzed by HPLC. When the reactions were under vacuum, the vacuum was quenched with argon before sampling.

Typically four simultaneous reactions were run; the first reaction was a control containing pivalic acid and MEEtOH only, the second one contained the acid and the alcohol plus a catalytic amount of alanine, the third one contained a catalytic amount of $Ti(OBu)_4$ instead of alanine, and the fourth contained both alanine and $Ti(OBu)_4$, Table 5.1

Table 5.1. Pivalic acid esterification.

| Reaction number | Reagents in mmol | | | |
|---|---|---|---|---|
| | PVA | MEEtOH | ALA | $Ti(OBu)_4$ |
| 1 | 20 | 20 | 0.00 | 0.00 |
| 2 | 20 | 20 | 0.49 | 0.00 |
| 3 | 20 | 20 | 0.00 | 0.29 |
| 4 | 20 | 20 | 0.47 | 0.29 |

Chromatography of Reaction Mixtures

Samples of the reaction mixture were collected (0.05-0.10 cc), diluted to 4.0-5.0 cc with HPLC methanol and filtered through 0.45μ Millipore filters. Samples containing $Ti(OBu)_4$ were passed through a 1 cm layer of alumina (80-20 mesh) on a 2.3 cm o.d. coarse pore sinter glass funnel, and filtered again through a 0.45 μ filter. The analysis was performed in a liquid chromatograph, described previously, using a 6/4 mixture of acetonitrile/water as solvent at a flow of 0.5 ml/min. Acid ester ratios were calculated by the respective areas measured at 215 nm. Figure 5.1 shows HPLC chromatograms for samples taken at diferent times from from the esterification reaction of pivalic acid.

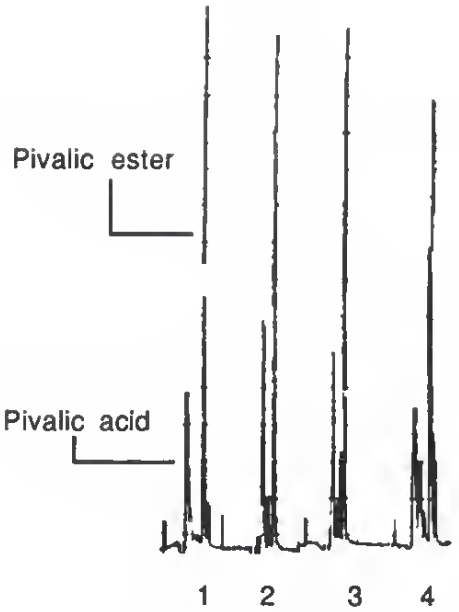



Figure 5.1. HPLC of pivalic acid esterification.

## Transesterification of Methyl Benzoate. Model Studies

### Transesterification Reactions

Transesterification reactions were carried out in a similar way as the esterification of pivalic acid. In order to assure uniformity in the four reactions run simultaneously, a new glass line was designed, see Figure, consisting of a horizontal tube connected to a cold trap in one end and a three way stopcock on the other and four outlets in between. Each reaction flask ( 50 cc, 3N round bottom) was attached to the line through 25.0 cm vertical tubes. The horizontal tube was wrapped with a heating tape, set at 120°C, to assure evaporation of the methanol liberated in the trans esterication. Reactions were carried out at RT under vacuum or

heated to the refluxing temperature, under argon. Samples were syringed out through a septum, purified in the same way as the pivalates and analyzed by HPLC at 230 nm or by GC. A typical set of reactions, is presented in Table 5.2.

Table 5.2. Methyl benzoate transesterification

| Reaction number | Reagents in mmol | | | |
|---|---|---|---|---|
| | Me Bz | MEEtOH | ALA | $Ti(OBu)_4$ |
| 1 | 20 | 20 | 0.00 | 0.00 |
| 2 | 20 | 20 | 0.00 | 0.15 |
| 3 | 20 | 20 | 0.34 | 0.00 |

## Chromatography of Transesterification Reactions

### High performance liquid chromatography

Samples of the reaction were purified and analyzed by HPLC under the same conditions as the pivalate samples, except for the maximum absorption wavelength, 230 nm for the benzoate as opposed to 215 for the pivalate, see Figure 5.2.

A sample of the transesterification product was collected from the HPLC effluent and used for mass spectrometry.

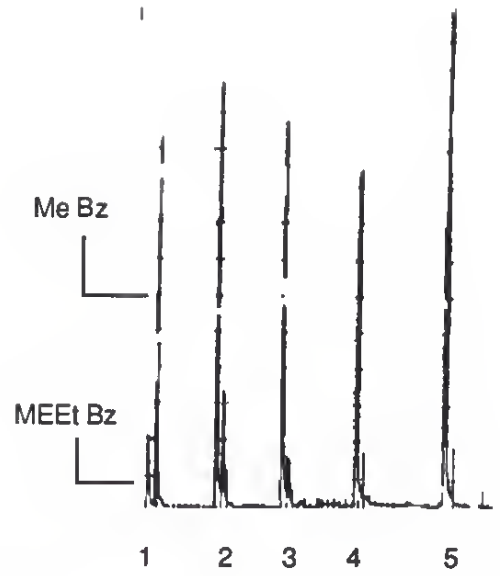



Figure 5.2. HPLC of Transesterification of methyl benzoate.

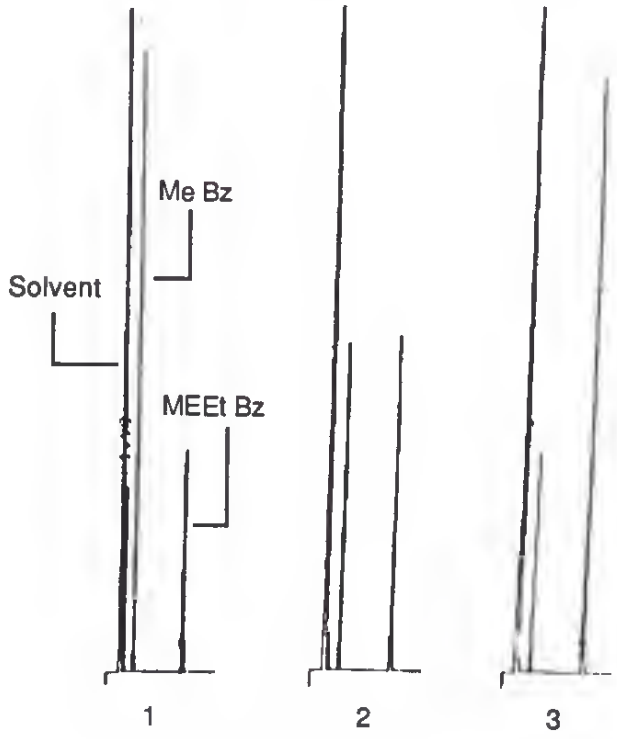



Figure 5.3. GLC of Transesterification of methyl benzoate.

Gas liquid chromatography

Samples of the transesterification, 0.05-0.1 ml, were purified as before, diluted with acetonitrile and injected, 1.0 µl, into a 5880A Hewlett Packard GC under the following conditions: injector at 300°C, detector at 320°C, oven T program, 100°C for 3min., ramp 20°/min to 200°C (2min), ramp 30°/min to 300°C (10min). Elution time for 2(2-methoxyethoxy)ethyl-benzoate: 8.55 min, see Figure 5.3.

Characterization of 2-(2-Methoxyethoxy)ethyl Benzoate

This ester is a colorless, viscous liquid, b.p.= 190°C

$^{1}$H NMR(δ,ppm): 3.40,s,3H, O$\underline{CH_3}$; 3.56,m,2H, and 3.70,m,2H, $CH_2$ of the methoxyethoxy moiety, 3.85 and 4.50,t,2H each,(j=7Hz), of the ethyl segment.

$^{13}$C NMR(δ,ppm): 58.4, O$\underline{CH_3}$; 64-72, five signals corresponding to five methyleneoxy; 128-136, six signals corresponding to the six phenyl carbons; 166.4, $\underline{C}$=O.

M.Sp.(CI,m/e, %I): 225(0.07); 194(0.09); 179(1.10); 149(27.05); 105(100); 77(50.18); 58(93.19).

IR(Neat) : 2870(s), C-H str. ; 1715(s), C=O str. ; 1100,1270(s), C-O str.

## Synthesis of Siloxane Random Copolymers

### Synthesis of Poly(dimethyl-co-methylcyanopropylsiloxane)

Methylcyanopropyldichlorosilane (10) (3.1 cc, 0.017 mol) and dimethyldichlorosilane (9) (79.5 cc, 0.62 mol), were mixed in diethylether (180 cc) in an addition funnel, attached to a 3 neck flask, with a drying tube on top, see Figure 5.4. This solution was added dropwise, over a period of three hours, to ice cold water (250 cc) under magnetic stirring. The other two necks of the flask were used as inlet and outlet for nitrogen gas. After the addition was finished, the reaction mixture was left stirring overnight at room temperature and then transferred to a 1 L separatory funnel. The water phase was drained off and the ether layer washed with deionized water (2x100 cc). The ethereal solution was rotaevaporated affording 56.0 g of a cloudy oil in the flask, and 27.0 g of a colorless oil in the solvent guard (cyclic dimethylsiloxane by $^1H$ NMR). The cloudy oil was used as obtained for the next reaction, hydrolysis with aqueous sulfuric acid; a small aliquot (0.3652 g) of

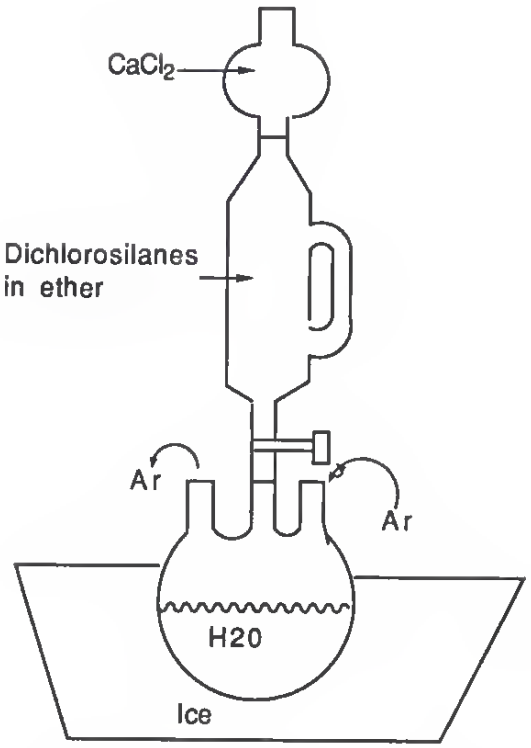



Figure 5.4. Apparatus for aqueous polymerization of dichlorosilanes.

this oil was dried using toluene to form the azeotrope, obtaining 0.2051 g of a colorless oil, allowing calculation of the total dry weight of the product as 31.5 g, 32.4 % yield. The dry sample was used to run IR and NMR spectra with the following results:

IR ($cm^{-1}$) : 2920, 2870, C-H str.; 2230, CN str.; 1050,Si-O-Si str.; 780, Si-C str.

$^1H$ NMR : 0.0 strong signal, $(CH_3)_2$-Si; 0.6, 1.6-2.3, $CH_2$'s of the cyanopropyl moiety.

Synthesis of Poly(dimethyl-co-methylcarboxypropylSiloxane) (11a)

The product from the above reaction (30.0 g) was treated with 105 cc of 50 % aqueous sulfuric acid in a 500 cc round bottom flask, at 106 °C for 12 hrs with magnetic stirring. The product, still hot, was decanted and washed with water (3x50 cc) affording a transparent gum wich was left stirring overnight with ether (300 cc). An aliquot (25 cc) was dried with anhydrous calcium sulfate, the solvent evaporated, affording 1.723 g of a colorless oil which was used for characterization of the product as follows:

IR: 3500-2700 broad band, hydrogen bonded O-H str.; 1700(m), C=O str.; 1050, Si-O-Si str; 780, Si-C str.

$^1$H NMR:0.0,s; 0.6,m; 1.24,m; 2.4 t(j=7 Hz);

GPC: $M_n$ = 6500, PS standard.

VPO(toluene, 50°C): $M_n$ = 4600

Synthesis of Siloxane Potassium Carboxylate (11b)E

A sample of the product from the above reaction (6.31 g) was transferred to a 2 L separatory funnel and diluted to 1.0 L in ether. Aqueous potassium hydroxide ( 20 cc, 10M), was added and the mixture shaken for 5 min. The aqueous layer was drained off and the ether layer washed with water (40x100 cc) to neutrality. There was formation of emulsions, every washing required long standing times and the aqueous phase was successively transferred to smaller separatory funnel to improve the extraction. The ether layer was dried with anhydrous sodium sulfate, evaporated under vacuum (0.1mm Hg) until most of the water was eliminated, then toluene

was added to help eliminating more water through the formation of the azeotrope, obtaining a milky gum. Finally this gum was freeze dried (liquid nitrogen) using benzene and a high vacuum line using 3 freeze-vacuum thaw cycles.

Synthesis of End-capped Siloxanes from Cyclic Monomers

Octamethylcyclotetrasiloxane (20 cc, 64.4 mmol) tetramethyl-tetracyanopropylcyclosiloxanes (mixture of 6 and 8 membered rings, 0.75 cc, 1.74 mmol), hexaphenyldisiloxane (0.48 g) and aqueous sulfuric acid (20 cc, 50 %) were combined in a 50 cc 3 neck flask and refluxed at 110 °C under magnetic stirring for 14 hrs. The product was decanted while still hot, washed with water (2x20 cc), dried under vacuum to eliminate the cyclics and left standing overnight. A white solid precipated out from the oil and after recrystallization with diethylether it was identified as hexaphenyldisiloxane. The crystallization was repeated until no more solid was obtained and the polysiloxane was characterized as follows:

IR ($cm^{-1}$): 3500-2700 broad band, H-bonded O-H and C-H str.; 1710, C=O; 1050, Si-O-Si str.; 760, C-Si str.

$^1H$ NMR (δ, ppm): 0.0, s, $CH_3$-Si; 0.6, 1.6, 2.2, $CH_2$'S of the propyl moiety; 7.2,m, and 7.4,d, of the phenyl ring. End group analysis allowed calculation of $M_n$ = 8800.

GPC: $M_n$ = 15000, PS standard.

## Grafting of Lactones and Lactams to Poly(siloxane)s (11a) and (11b)

### Grafting of Pivalolactone (8)

The potassium salt of the polysiloxane (5.0 g), recently dried in a 100 cc round bottom flask equipped with a rota-flo stopcock, was introduced in a dry box where it was dissolved in THF (75 cc) under magnetic stirring; pivalolactone (2.15 cc) and 18-crown-6 (0.01 g) were added and the reaction mixture left stirring overnight. A gel-likeproduct was obtained, insoluble in all common organic solvents, very slowly soluble in m-cresol, under constant stirring. The bulk of the product was successively extracted with ether, methylene chloride and acetone by stirring with the solvent for 10 hrs in each case. Finally it was rinsed with m-cresol, ether, dried under vacuum, and characterized as follows:

1H NMR (HFIpr) : 0.0, s, $\underline{CH_3}$-Si; 1.1 and 4.0, two singlets, $CH_3$'s and $CH_2$ of the pivalolactone moiety.

$^{13}C$ NMR (HFIpr) : 0,0, 21.5, 42.5 plus 176.5, C=O fo the lactone.

The product obtained above resulted from a mixture of a 7/3 polysiloxane/pivalolactone w/w ratio. The same procedure was successfully applied for the preparation of a graft with a polysiloxane/pivalolactone ratio of 3/7.

Grafting of Δ-Valerolactone (39)

Freshly distilled δ-valerolactone (1.0 cc) was mixed, in a dry box, with 10.0 cc of a THF solution containing 1.0 g of polysiloxane potassium carboxylate and 0.01 g of 18-crown-6, left stirring at room temperature for 2 hrs with no apparent reaction. The temperature of the reaction was gradually increased to 40, 60, 80 and 90°C with constant stirring. At this final temperature polymerization was apparent as the viscosity of the solution increased. Analysis of the product by TLC, NMR, IR and GPC confirmed formation of the graft as follows:

IR: 1720, C=O str.; 1255 C-O str.; 1050, Si-O-Si str.; 800, Si-C str.

$^1$H NMR: 0.0,s, $\underline{CH_3}$-Si; 1.6,m, $CH_2\underline{CH_2}$; 2.3,m,$\underline{CH_2}CO$; 4.0,m, $\underline{CH_2}O$.

GPC (THF, 1.0 cc/min): $M_n$ = 15300 vs 6500 of the polysiloxane used as startitng material.

TLC ($CHCL_3$/ETOAC, 9/1, $SiO_2$): Rf= 0.83 for graft, 0.91 for siloxane, 0.20 for δ-valerolactone.

Grafting of E-Caprolactam (43)

E-caprolactam recrystallized in cyclohexane ( 0.65 g) was introduced in a thick wall (2 mm), long neck (25.0 cm) glass tube, through a long stem funnel, polysiloxane with pendant carboxylic acid groups ( 0.65 g) added with a long pipette and the mixture freeze dried (liquid nitrogen) with benzene, through 3 freeze-cool-thaw cycles. Water (0.3 cc) previously degassed, was vacuum

transferred to the reaction tube, which was then frozen with liquid nitrogen and sealed under vacuum. The sealed tube, with its contents, was heated in a sand bath to 250°C for 3 hrs, then cooled, opened, connected to a Schlenk line and reheated, under nitrogen, to 180°C for 2 hrs to eliminate the water. A white solid was observed at the bottom of the tube with a layer of a viscous solid on top. This reaction mixture was washed by leaving it stirring with diethyl ether overnight. The procedure was repeated with dichloromethane leaving a white solid in the tube. Evaporation of the ether and dichloromethane extracts afforded 0.475 g and 0.068 g, respectively, of a viscous oil which was found to be a mixture of polysiloxane and ε-caprolactam by $^1$H NMR. The solid remaining in the tube ( 0.75 g) was insoluble in most common organic solvents but soluble in m-cresol and hexafluoroisopropanol; one third of the product was dissolved in m-cresol and recristallized 3 times by adding acetone. The solvent was removed by centrifugation, washed 3 times with acetone, dried in a vacuum oven, at 40°C, for 10 hrs.

Film Casting of Siloxane-Lactam Graft Copolymers

Films of the graft copolymer were easily obtained by pouring a 2 % solution of the copolymer in m-cresol over a Petri dish. These films, partially transparent, with a very smooth surface, contained some residual m-cresol that could not be removed completly even after drying them at 40°C, under vacuum, for 24 hrs. The casting was repeated using hexafluoroisopropanol as solvent; no residual solvent was left after drying as before, as confirmed by the absence

of fluorine in the surface XPS analysis. These fims were directly used for IR spectroscopy , and surface analysis.

Characterization of the copolymer was carried out as follows:

IR: 3260, N-H str. ; 2920, 2860, C-H str. ; 1625, C=O str. ; 1530, N-H bending; 1060, Si-O-Si str. ; 780 Si-C str. ; 675, N-H wag.

$^1$H NMR: 0.0,s, $CH_3$-Si; 1.6, m, $CH_2$'s of the polylactam, 2.3, t, $CH_2CO$; 3.2, t, $CH_2$-N; 7.3, b.s., N-H.

13C NMR: 32, 35, 43, corresponding to the intermediate $CH_2$'s of the lactam; 45, $\underline{C}H_2$-CO; 65, $\underline{C}H_2$-N, 183, $\underline{C}$=O.

X Ray photoelectron spectroscopy (XPS) :

Table 5.3. XPS data of a siloxane-lactam film.

| Element | Position (ev) | width (ev) | Quant Factor | Atomic mass | Atomic conc% | Mass conc |
|---|---|---|---|---|---|---|
| C1S | 285.05 | 2.04 | 1.00 | 12.01 | 61.12 | 46.67 |
| O1S | 532.20 | 1.89 | 1.71 | 16.00 | 18.06 | 18.37 |
| N1S | 399.95 | 1.86 | 1.42 | 14.01 | 2.48 | 2.21 |
| Si2P | 102.65 | 1.89 | 1.17 | 28.09 | 18.34 | 32.75 |

Water contact angle:

A drop of deinonized water was placed on the film and the surface angle on both sides of the drop was measured with a NRL C.A. goniometer, Table 5.4.

Table 5.4. Water contact angle for a film of siloxane-lactam graft copolymer

| Meas N° | Left angle | Right angle | Average |
|---|---|---|---|
| 1 | 89 | 93 | 91 |
| 2 | 94 | 95 | 95 |
| 3 | 88 | 88 | 88 |
| 4 | 88 | 88 | 88 |

Final average : 90.5°

## Molecular weight Determinations

### Vapor Pressure Osmometry

The reference and sample cells of a Wescan 233 vapor pressure osmometer, were washed with freshly distilled toluene and excess solvent drain off with a syringe; this operation was repeated 3 times. The controls were set as follows: current = 20, range = 2, temperature = 2 (coarse), 300 (fine). The temperature was stabilized at 50°C and the solvent average voltage was 1.4 mV. Sucrose octaacetate (Wescan Instruments) was used as standard to calculate the calibration factor K (from the equation $\Delta V = KC_2/m_2$), K= 2260, from a calibration curve obtained by plotting $\Delta V/C$ vs C for 4 solutions, in toluene, with concentrations ranging from 0.77 to 6.80 g/cc; $\Delta V$ is voltage change, $C_2$ and $m_2$ are concentration and molecular weight of the solute, respectively.

This calibration was tested with a polystyrene standard with $M_n$ = 12,000 obtaining an experimental value of $M_n$ = 10,800, with a

10% error. As an illustration of the use of VPO for the determination of molecular weights, the data, Table 5.5, and corresponding plot, Figure 5.5, for this polystyrene standard are presented next.

Table 5.5. VPO for PS standard

| C(g/L) | ΔV | ΔV/C |
|---|---|---|
| 15 | 3.6 | 0.24 |
| 20 | 5.4 | 0.17 |
| 30 | 8.4 | 0.28 |
| 40 | 12.3 | 0.31 |

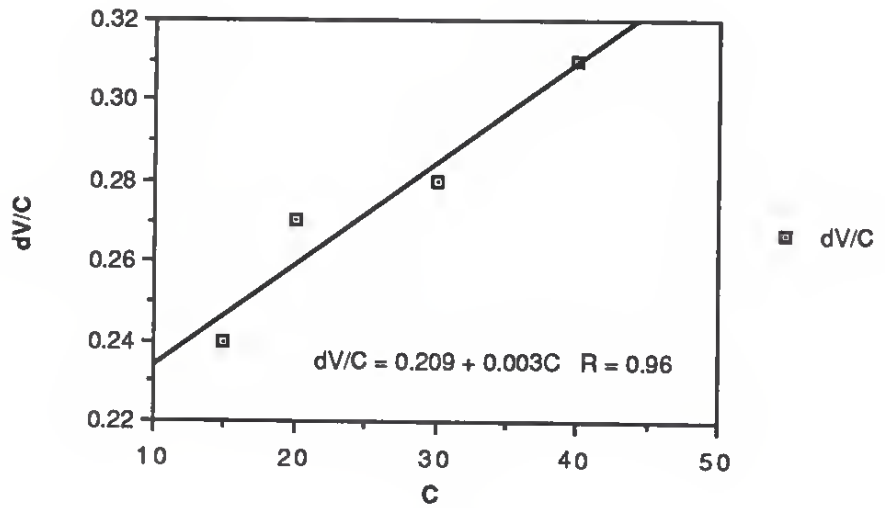



Figure 5.5. VPO for PS standard.

From the previous graph the intersect 0.209 is obtained then,

$0.209 = K/Mn$ or $Mn = K/0.209 = 2{,}260/0.209 = 10{,}813$

Using the same method for the polysiloxane carboxylic acid a number average molecular weight of 5000 was calculated.

Gel Permeation Chromatography

Two calibraton curves were obtained by plotting ln M vs V, where M is molecular weight at the crest of the signal and V is elution volume in cc., using narrow MW distribution polystyrene standards (Sci. Polym. Products). In the first calibration curve, Table 5.6 and Figure 5.6, standards with molecular weights of 97200, 37000, and 17500 were used.

Table 5.6. Data for PS with higher molecular weight.

| Standard | Mp | Mw/Mn | ln Mp | Vmax (cc) |
|---|---|---|---|---|
| PS 17K | 17500 | 1.06 | 9.77 | 14.83 |
| PS 37K | 37000 | 1.06 | 10.52 | 13.97 |
| PS 97K | 97200 | 1.02 | 11.48 | 13.47 |

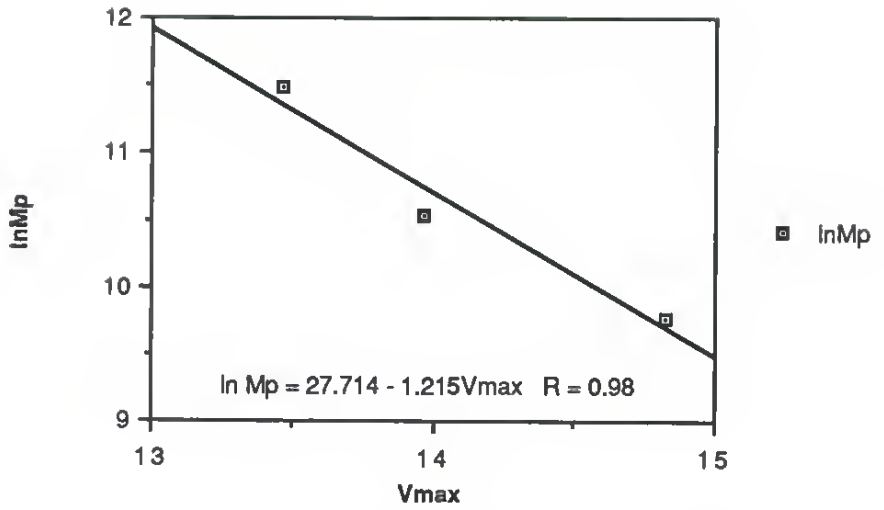



Figure 5.6. Calibration curve for PS with higher molecular weight.

Standards with molecular weights of 4000, 1681, and 781, were used in the second calibration curve, table 5.7 and Figure 5.7.

Table 5.7. Data for PS with lower molecular weight.

| Standard | Mp | Mw/Mn | ln Mp | Vmax (cc) |
|---|---|---|---|---|
| PS 781 | 781 | 1.14 | 6.66 | 20.00 |
| PS 1.6K | 1681 | 1.06 | 7.43 | 18.98 |
| PS 4K | 4000 | 1.06 | 8.29 | 17.37 |

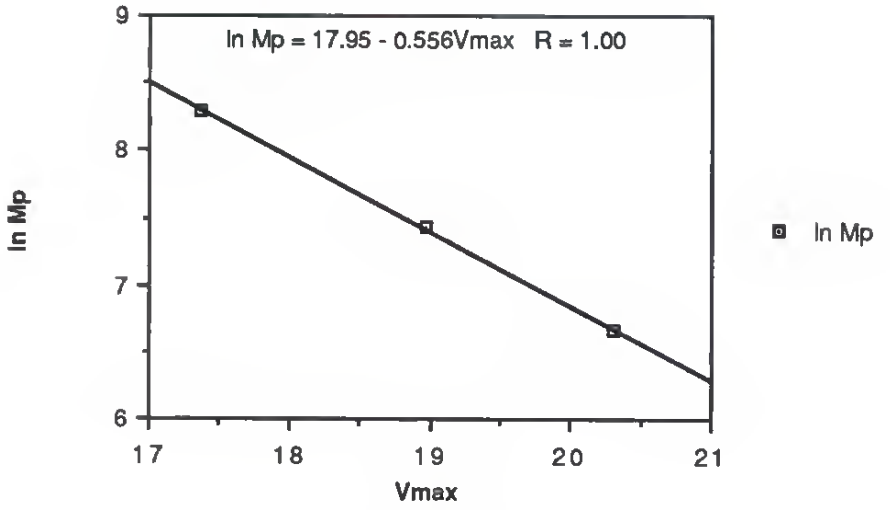



Figure 5.7. Calibration curve for PS with lower molecular weight.

These calibration curves were used to calculate the molecular weights of the polysiloxanes synthesized. A list of polysiloxanes carboxylic acids with their GPC molecular weights is given in Table 5.8.

Table 5.8. Mn of polysiloxanes by GPC

| Sample | Mn |
|---|---|
| Sil52791 | 4600 |
| Sil58291 | 28290 |
| $Ph_3$Sil61391 | 67370 |

The label for each sample includes the date when it was synthesized, $Ph_3$ indicates that $(Ph_3Si)_2O$ was used as end capper.

Universal Calibration for Molecular weights

In order to construct a Universal calibration curve a combination of viscometry and GPC was necessary. Polystyrene standards from different suppliers were used as follows :

($M_n$, brand) : 7400, SPP; 16827, SPP; 37000, PCC; 68000, SPP; 149500, SPP; 773000, WA, where SPP = Scientific Polymer Products, PCC = Presure Chemical Company, WA = Water Associates.

GPC of the samples was performed in a liquid chromatograph described before, measuring the elution volume (Ve) of each one of the standards.

Viscometry was carried out as follows: Using a Ubbelohde capillary viscometer, elution times of the solvent and of four different concentrations for each standard were measured with a stop watch to 1/100 of a second. The viscometer was inmersed in a water bath at 25.0°C (measured with a 0-50°C thermometer, 0.1° graduation) topped with polyurethane chips to avoid water evaporation. The temperature was controlled by circulating tap water (23°C) through a copper spiral placed inside the water bath, equipped with a Haake E-52 thermostatt. The solvent, THF, was filtered through 0.45 μ Millipore filters, before use. Solvent and solutions were equilibrated in the bath for 10 minutes before measurements. Data for viscosity measurements of some of these sample is given in table 5.9. The intersect of a plot of $\eta_{spec}/C$ vs C shown in Figure 5.8, corresponds to the intrinsic viscosity, $[\eta] = 37.22$, which is then used

for universal calibration. The same procedure is followed for each one of the polystyrene standards and then a plot of log(Mn[η]) vs Ve (elution volume) produces a universal calibration curve that allows calculation of absolute molecular weights.

Table 5.9. Viscosity data for Polystyrene, Mn : 79000

| C(g/L) | 0.411 | 0.753 | 1.04 | 1.29 |
|---|---|---|---|---|
| $\eta_{rel}$ | 1.016 | 1.030 | 1.042 | 1.053 |
| $\eta_{spc}$ | 0.016 | 0.030 | 0.042 | 0.053 |
| $\eta_{red}$ | 38.21 | 39.56 | 39.89 | 40.73 |

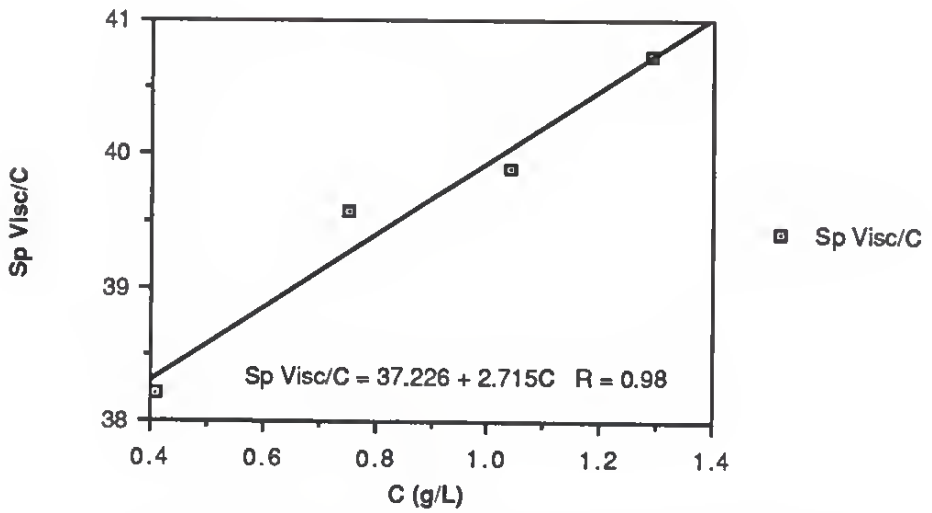



Figure 5.8. Spec. Visc./C vs C plot for PS 79000.

The same procedure is followed for each one of the polystyrene standards and then a plot of log(Mn[η]) vs Ve (elution volume) produces a universal calibration curve that allows calculation of

absolute molecular weights. The data for a universal calibration and the corresponding curve are shown in Table 5.10 and Figure 5.9.

Table 5.10. Data for Universal calibration curve using PS standards.

| Mn | [η] | log[η]Mn | Ve |
|---|---|---|---|
| 830000 | 65.88 | 7.74 | 9.82 |
| 139000 | 57.69 | 6.90 | 10.83 |
| 79000 | 37.32 | 6.47 | 11.38 |
| 37000 | 24.09 | 5.94 | 12.18 |
| 17400 | 12.39 | 5.53 | 13.05 |
| 7700 | 7.26 | 4.75 | 14.28 |

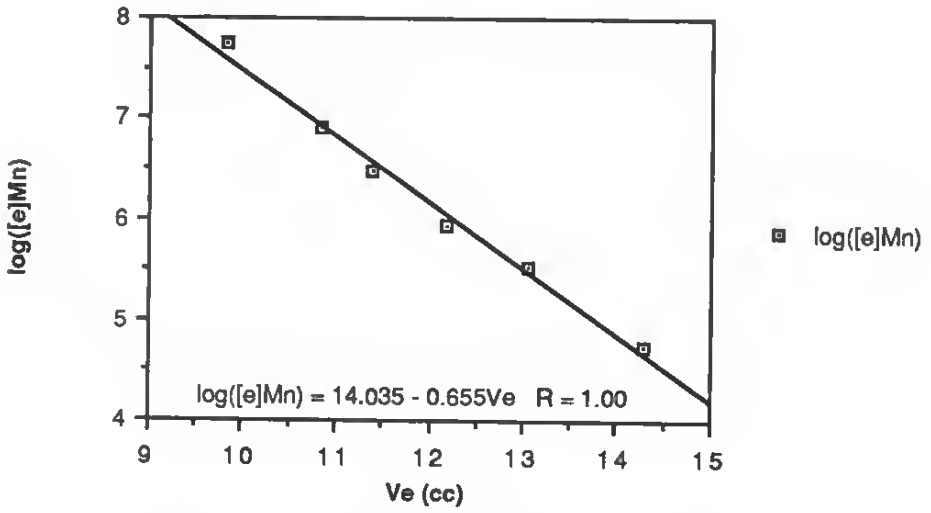



Figure 5.9. Universal calibration curve.

End Group Analysis

End group analysis was only possible for polysiloxanes end-capped with hexaphenyldisiloxane by using $^1H$ NMR. The ratio of $(CH_3)_2Si$ protons to the phenyl protons of the end groups was used to calculate the number average molecular weight of the polysiloxane. The data for one sample of polysiloxane-carboxylic acid is given in Table 5.11.

Table 5.11. 1H NMR data for end group analysis of End capped polysiloxane carboxylic acid

| Chem shift (ppm) | Assignment | Integration |
|---|---|---|
| 0.00 | $(CH_3)_2Si$ | 167.3 |
| 0.44 | $CH_2Si$ | 0.7 |
| 1.83 | $CH_2CH_2COOH$ | 1.1 |
| 2.23 | $CH_2COOH$ | 1.6 |
| 7.6-7.0 | $Ph_3Si$ | 2.7 |

Assuming that both ends of the polysiloxane are capped with triphenyl silyl groups :

$$Ph_3Si\text{-}O\text{-}[(CH_3)_2Si\text{-}O]_n\text{-}[CH_3Si(CH_2)_3COOH]_m\text{-}OSi\text{-}PH_3$$

From Table 5.11,

$$A/H = 2.7/30 = 0.09$$

Number of $HOOC(CH_2)_3\ SiCH_3$ groups = $1.1/(0.09 \times 2) = 6.1 = m$

Area for $(CH_3)_2Si$ = 167.3 - 6.1x 0.09x3 = 165.6

Number of $(CH_3)_2Si$ = 165.6/(0.09x6) = 306.7 = n

Mn = 275 + 74x88.8 + 146x25.5 + 259 = 24,143

n/m = 306.7/6.1 = 27/1 corresponds to the ratio of dimethyl siloxane to methylcarboxypropyl siloxane units.

Microscopy

Microscopy was performed with a Nikon microscope. A film of poly(siloxane-g-ε-caprolactam) was observed under 90° polarized light, 7 volt, 40x10 enhancement.

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Hector Fabio Zuluaga was born on April 16, 1946, in Anserma, a small town on the Andes of Colombia. He began his undergraduate work at the Universidad del Valle at Cali, Colombia, where he received his Bachelor of Science degree in June 1969. Shortly afterwards, he was appointed as a Chemistry Instructor at the same University, and after one year he moved to the Universidad Tecnologica de Pereira, where he worked as an Auxiliary Professor for three years. In July 1973 he was awarded a British Council Scholarship to pursue a Master of Science degree at the University of Manchester in England. Upon completion of this degree, in September 1975, returned to the Universidad Tecnologica de Pereira, where he stayed for two more years and then went on to the Universidad del Valle in November 1977 as an Assistant Professor. In August 1988 he came to the University of Florida, where he began his graduate research with Dr K. B. Wagener until he received his Ph.D. in 1993.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Professor of Chemistry

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